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A study of the decomposition of some aromatic diazonium hexafluorophosphate salts.

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A STUDY OF THE DECOMPOSITION OF SOME AROMATIC

DIAZONIUM HEXAFLUOROPHOSPHATE SALTS

BY

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A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
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ABSTRACT

In order to open new routes to the synthesis of aromatic fluorides many modifications based on the classical Schiemann Reaction have appeared in the literature in the last fifteen years. These methods are discussed and a new modification is presented in this work. The substitution of hexafluorophosphoric acid for fluoboric acid in the Schiemann Reaction was found to lead in almost every case to increased yields of fluoroaromatic. A quite marked improvement was noted in the preparation of ortho and para-fluorobenzoic acids and in the synthesis of o-bromofluoro-benzene. A comparison of the yields obtained by the hexa-fluorophosphate method to those obtained via the normal Schiemann Reaction is included.

In the course of work on the preparation of arylfluo-rides a new method for the reduction of diazonium compounds was discovered. Tetramethylurea was found to reduce these compounds. Its use has several advantages over the standard methods. The reaction is spontaneous, simple to perform, and one of the few reductions of diazonium compounds that can be carried out in non-aqueous media. Greatly increased yields of reduction product are obtained from ortho and para-aminobenzoic acids over the usual deamination proce-dures by this method.

A new compound, o-methylphenoxytetramethylamidinium hexafluorophosphate, was isolated from the attempted reduction of o-toluenediazonium hexafluorophosphate in tetramethylurea. The structure of this compound was proved by elemental analysis and hydrolysis to o-cresol and dimethylamine.

ACKNOWLEDGEMENTS

I wish to acknowledge, with thanks, the direction and encouragement given me by Dr. K.G. Rutherford during the course of this work.

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iv

TABLE OF CONTENTS

v

LIST OF TABLES

LIST OF ILLUSTRATIONS

A Study of the Decomposition of Some Aromatic
Diazonium Hexafluorophosphate Salts

CHAPTER I

INTRODUCTION

1. The Replacement of an Aromatic Amino Group by Fluorine.

Aryldiazonium salts are useful intermediates in the preparation of several classes of organic compounds. Such salts are precursors in the following synthetic procedures:

a) The preparation of phenols by the hydrolysis of a diazonium salt.

b) The preparation of aryliodides, bromides, chlorides, nitriles and thiocyanates by the Sandmeyer Reaction.

c) The replacement of the diazonium group by -SH, N_3, and $-SCH_2COOH$.

d) The preparation of nitroaromatics.[1,2]

e) The introduction of arsonic or stibonic acid groups by the Bart Reaction.

f) The preparation of fluoroaromatics by the Schiemann Reaction.

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1 E.B. Starkey, J. Am. Chem. Soc., 59, 1479 (1937).

2 H.H. Hodgson and E. Marsden, J. Chem. Soc., 22 (1944).

1

g) The preparation of arylphosphonic or diarylphosphinic acids.[3]

h) The preparation of aromatic compounds of mercury,[4] tin,[5] lead,[6] bismuth,[7] and antimony.[8]

i) The replacement of the diazonium group by hydrogen.

j) Aryl coupling reactions - the Bachmann-Gomberg Reaction.

k) Arylation reactions - Meerwein Arylation.

l) The preparation of azo compounds by coupling with phenols and aromatic amines.

m) The preparation of anilides.[9]

n) The preparation of organo-thallium compounds.[10]

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3 G.O. Doak and L.D. Freedman, J. Am. Chem. Soc., 73, 5658 (1951).

4 A.N. Nesmeyanov, Ber., 62, 1010 (1929).

5 A.N. Nesmeyanov, K.A. Kocheskov, and V. A. Klimova, Ber., 68, 1877 (1935).

6 K.A. Kocheskov, A.N. Nesmeyanov, and N.K. Gipp, J. Gen. Chem., (USSR), 6, 172 (1936). C.A., 30, 4834 (1936).

7 H. Gilman and H.L. Yablunky, J. Am. Chem. Soc., 63, 949 (1941).

8 G.O. Doak and H.G. Steinman, ibid., 68, 1987 (1946).

9 L.G. Makarova and A.N. Nesmeyanov, Isvest. Akad. Nauk., SSSR, Otdel. Khim. Nauk., 1019 (1954). C.A., 50, 241 (1956).

10 A.N. Nesmeyanov and L.G. Makarova, Doklady Akad. Nauk., SSSR, 87, 417 (1952). C.A., 48, 622 (1954).

o) The preparation of arylgermanium[11] and arylselenium compounds.[12]

In many of the above reactions the isolation of the intermediate diazonium salt is not a necessary requirement for the realization of good yields of products. In others, however, isolation of the intermediate salt is either desirable or necessary in order to obtain respectable conversion in the overall reaction. Thus in the Schiemann Reaction (Fig. 1) which involves the replacement of a primary amino group with a fluorine atom it is of prime importance to isolate and purify the diazonium fluoborate in order to obtain good yields of the fluorocarbon derivative.

$$\text{C}_6\text{H}_5\text{-N}{\equiv}\text{N}]\ \text{BF}_4 \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{-F} + \text{N}_2 + \text{BF}_3$$
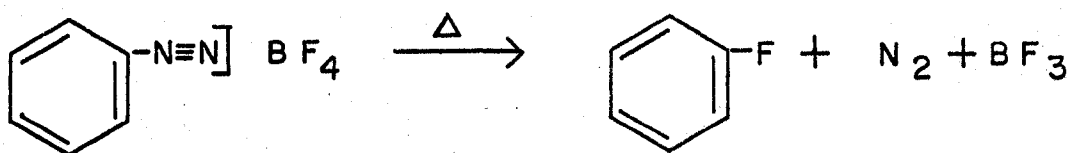
Fig. 1 The Schiemann Reaction.

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11 A.N. Nesmeyanov, L.I. Emel'yanova and L.G. Makarova, Doklady Akad. Nauk., SSSR, 122, 403 (1958). C.A., 53, 3115 (1959).

12 A.N. Nesmeyanov, V.N. Vinogradova, and L.G. Makarova, Isvest. Akad. Nauk., SSSR, Otdel Khim. Nauk., 1710 (1960). C.A. 55, 8335 (1961).

The Schiemann Reaction is of great interest in organic chemistry since it is the classical procedure used for the preparation of all types of aromatic fluorocarbons. Indeed, with a few unique exceptions it is the only method available for the incorporation of the fluorine atom into an aromatic nucleus. The reaction is characterized by its simplicity of operation which involves routine diazotization of an aromatic amine followed by the addition of fluoborate ion. Invariably the diazonium fluoborate is relatively insoluble in the reaction medium and is obtained as a crystalline salt. This in itself is quite unique since diazonium compounds in general are unstable even in solution at temperatures slightly above 0°. The fluoroborates, however, can be washed with water and even recrystallized from aqueous solution in order to remove traces of impurities which affect the yield of the final decomposition stage in the overall procedure. The pyrolysis of the fluoborate usually proceeds smoothly to yield the aromatic fluoride, nitrogen, and boron trifluoride.

The success of the latter step in the Schiemann Reaction is very sensitive to traces of impurities. Since the diazotization step usually involves generation of nitrous acid by the action of hydrochloric acid on sodium nitrite, chloride ion is usually a contaminant as a result of coprecipitation of sodium chloride with the fluoborate. Several cases have been reported whereby a chlorine atom has been incorporated into the aromatic nucleus. Thus

Finger[13] found that 2,5-difluorochlorobenzene and 2,4-di-
fluorochlorobenzene were obtained when 2,4-difluorobenzene-
diazonium fluoborate was decomposed. It was found that
the chlorine atom originated from sodium chloride that had
coprecipitated with the fluoborate. Careful washing of the
diazonium salt eliminated this undesirable side reaction.
Again, the presence of traces of water reduces the yields
of fluoroaromatic by hydrolysis which produces phenolic
derivatives.

The purification of diazonium fluoborates usually in-
volves copious washing with cold, distilled water. The
salt is usually air-dried followed by drying in vacuo to
remove the last traces of moisture. If the diazonium salt
is appreciably soluble in water the above purification
procedure becomes very limited and total removal of foreign
ions is not realized. Overall yields are then decreased
substantially.

The mechanism of the thermal decomposition of aryl-
diazonium fluoborates has been studied by several workers.
However only tentative suggestions for either a free rad-
ical or ionic mechanism have thus far been proposed. These
are discussed by Roe[14] in an article on the Schiemann
Reaction published in Organic Reactions. (See Fig. 2).

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13 G.C. Finger and R.E. Oesterling, J. Am. Chem. Soc.,
78, 2593 (1956).

14 A. Roe, in Organic Reactions, (New York, 1949),
Vol. 5, p.193.

$$Ar:N\equiv N]^{+} \; [\ddot{F}:BF_3]^{-} \quad \xrightarrow{\Delta}$$

1. Carbonium ion.

$$Ar^{+} \quad + \quad N_2 \quad + \quad [\ddot{F}:BF_3]^{-\cdot}$$

$$Ar^{+} + \; [\ddot{F}:BF_3]^{-} \longrightarrow Ar:\ddot{F}: \; + \; BF_3$$

2. Free radical.

$$Ar\cdot \quad + \quad N_2 \quad + \quad BF_3 \quad + \quad \cdot\ddot{F}:$$

$$Ar\cdot \quad + \quad \cdot\ddot{F}: \quad \longrightarrow \quad Ar:\ddot{F}:$$

3. Rearrangement.

$$\begin{bmatrix} Ar & \longrightarrow & :N\equiv N: \\ \nwarrow & & \\ :\ddot{F}: & & \\ \nwarrow & & \\ \ddot{B}F_3 & & \end{bmatrix} \longrightarrow Ar:\ddot{F}: + \; N_2 + BF_3$$
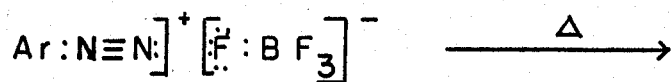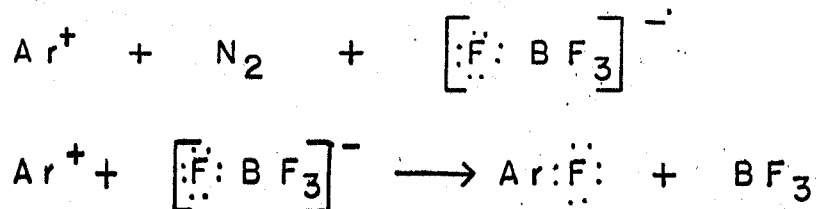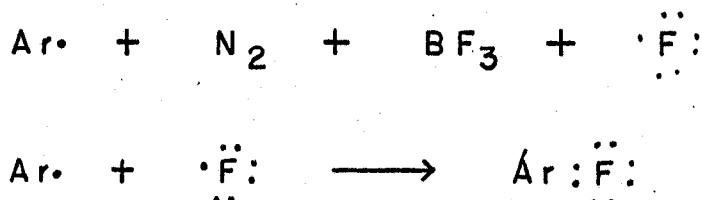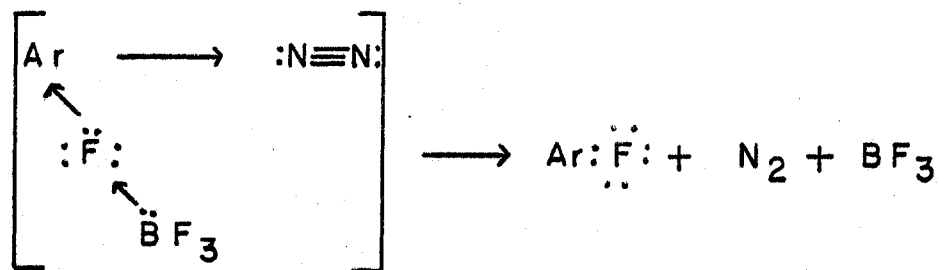
Fig. 2. Proposed mechanisms for the decomposition
of aryldiazonium fluoborates - from Roe.

Since the time of publication of this article Nesmeyanov,
Makarova and their co-workers[15-18] have reported the

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15 A.N. Nesmeyanov and L.G. Makarova, Bull. Acad. Sci.,
URSS, Classe sci. chem., 213 (1947).

16 L.G. Makarova and M.K. Matveeva, ibid., 565 (1958).

17 L.G. Makarova and E.A. Gribchenko, ibid., 693 (1958).

18 L.G. Makarova, M.K. Matveeva, and E.A. Gribchenko,
ibid., 1399 (1958).

results of decomposition of diazonium fluoborates and diazonium chlorides in nitrobenzene. These authors have found that decomposition of aryldiazonium fluoborates in nitrobenzene yields m-nitrobiphenyl. This is the product that would be expected for an ionic intermediate and they concluded that a phenyl cation was formed during the decomposition. The decomposition of phenyldiazonium chloride in nitrobenzene gave a mixture of ortho, meta, and para-nitrobiphenyl. These results are indicative of a free radical mechanism. Similarly, Olah and Tolgyesi[19] have found that the decomposition of benzenediazonium fluoborates, chloroborates, and bromoborates in fluorobenzene yields ortho and para-fluorobiphenyl (as expected for an ionic mechanism) while the decomposition of the corresponding diazonium chlorides in the same solvent gives a mixture of all isomers (as expected for a free radical mechanism). As is pointed out by Olah, however, the results of his investigations are applicable only to decompositions at low temperatures (less than 85° in all cases) and in the presence of a solvent. Decompositions carried out without solvent and at higher temperatures could well be free radical in nature. In fact, this would probably be the preferred mechanism.

Since the Schiemann Reaction is the only general method available for the preparation of aromatic fluoride

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19 G. Olah and W.S. Tolgyesi, J. Org. Chem., 26, 2053 (1961).

compounds it is not surprising that this procedure has been the object of much research. Several modifications have been reported all of which are directed towards the improvement of yields. The problem is simplified in this respect since the overall reaction is carried out in only two separate stages. A modification which enhances the yield of one of the steps is almost certain to prove general for all classes of compounds.

The first way in which overall yields of the Schiemann Reaction could be improved would involve the use of methods that lead to isolation of greater amounts of the diazonium fluoborates. Several methods have been proposed which have proved quite fruitful. For example, amines which are poorly soluble in aqueous hydrochloric acid solution can often be more readily diazotized in a mixture of sulfuric and glacial acetic acids.[20] Lakin and Petrova[21] recently reported the preparation of anthraquinone-1-diazonium fluoborate in 87.5% yield via the formation of the aminosulfate followed by diazotization with fluoboric acid and aqueous sodium nitrite.

In some cases an advantage is realized in the preparation of diazonium fluoborates by the use of non-aqueous solvent systems. In these cases the diazonium salt may be

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20 H.H. Hodgson and J. Walker, J. Chem. Soc., 1620 (1930).

21 A.M. Lakin and G.S. Petrova, Zhur. Obshchei Khim., 27, 2171 (1957). C.A., 52, 6297 (1958).

prepared by the use of nitrosyl fluoborate[22] or the complex of boron trifluoride with dinitrogen trioxide.[23] A variety of alkyl nitrites have also been used for this purpose. The use of nitrosyl fluoborate has lead to the isolation of phenyldiazonium fluoborate, 2,4-dibromonaphthyl-1-diazonium fluoborate, and 2,6-dibromophenol-4-diazonium fluoborate in yields of 90, 48, and 100% respectively. The use of the dinitrogen trioxide-boron trifluoride complex is particularly advantageous in the conversion of weakly basic amines to the diazonium salt.

Diazotizations carried out in aqueous fluoboric acid and hydrofluoric acid have been found to give increased yields of the aromatic fluoride.[24] Thus fluorobenzene, p-bromofluorobenzene, o-fluoroanisole, and 1-fluoronaphthalene were prepared in overall yields of 66, 55, 62, and 57%, respectively, by this method. The addition of a solution of nitrosyl chloride dissolved in an excess of hydrofluoric acid to aniline, 2-aminopyridine, and m-toluidine leads to good yields of the corresponding fluorocompounds.[25]

22 U. Wannagat and G. Hohlstein, Ber., 88, 1839 (1955).

23 G.B. Bachman and T. Hokama, J. Am. Chem. Soc., 79, 4370 (1957).

24 J.D. Head and F.J. Jones, U.S. Pat., 2,606,183. C.A., 47, P3875 (1953).

25 W.J. Schenk and G.R. Pellon, U.S. Pat., 2,563,796. C.A., 46, P9125 (1952).

The preparation of arylfluorides via the decomposition of aryldiazonium fluorides in anhydrous hydrofluoric acid has been investigated by Ferm and VanderWerf.[26] The method involves diazotization of the aromatic amine in cold hydrofluoric acid and subsequent decomposition of the diazonium salt when the solution is warmed to the reflux temperature of hydrofluoric acid. The above workers reported the preparation of the following compounds by this method in the stated yields; fluorobenzene (82%), p-fluoro-toluene (78%), m-fluorotoluene (82%), o-fluorotoluene (78%), 4-fluoro-1,3-dimethylbenzene (57%), 2-fluoro-1,4-dimethyl-benzene (43%), m-fluorochlorobenzene (81%), p-fluorochloro-benzene (74%), m-nitrofluorobenzene (39%), p-nitrofluoro-benzene (62%), m-fluorophenol (46%), o-fluorobenzoic acid (57%), m-fluorobenzoic acid (78%), p-fluorobenzoic acid (98%), and o-fluorobiphenyl (82%). The method failed to give satisfactory results with amines which contained ortho substituents with one or more atoms with unshared electrons. Thus o-chloroaniline, o-aminophenol and o-anisidine failed to give satisfactory yields of the fluoride. The authors suggest this is because the diazonium fluorides derived from these compounds are too stable to decompose readily at the boiling point of hydrofluoric acid at atmospheric pressure. If the pressure was increased and the tempera-ture was raised to a point sufficiently high to decompose

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26 R.L. Ferm and C.A. VanderWerf, J. Am. Chem. Soc., 72, 4809 (1950).

the aryldiazonium fluorides,a complex mixture of high melting solids was obtained instead of the arylfluorides.

In addition to the above limitations in the scope of the reaction it also suffers from the well known disadvantages involved with the use of hydrofluoric acid. A monel metal flask and a stainless steel stirrer are required for diazotization in hydrofluoric acid. In addition a copper coil must be attached to this flask so that the diazonium fluoride may be heated to the reflux temperature of hydrofluoric acid and thus decomposed. A perhaps greater difficulty encountered in this procedure is the personal danger involved in work with hydrofluoric acid.

Diazonium fluosilicates have been prepared and used as intermediates in the Schiemann Reaction but in general the yields of fluorides obtained through their use are not as high as those obtained by the normal Schiemann conditions.[27,28] The results of these investigations are summarized in Table 1. As can be seen from the table, p-nitroaniline is the only amine which gives respectable yields of fluorocarbon and in every case except that of p-aminophenol the yield is lower than is obtained by the normal Schiemann Reaction.

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27 P.H. Check, R.H. Wiley, and A. Roe, J. Am. Chem. Soc., 71, 1863 (1949).

28 R.D. Beaty and W.K.R. Musgrave, J. Chem. Soc., 875 (1952).

Table 1

A Comparison of the use of Fluosilicate versus Fluoborate in the Schiemann Reaction

Amine	Percent Yield of Diazonium Fluosilicate	Percent Yield of Fluoroaromatic	Percent Yield of Fluoro- aromatic by Schiemann[a]	Ref.
Aniline	87	30.4		27
m-Nitroaniline	86	22.3	10-19	27
p-Nitroaniline	85	33.8	40-58	27
p-Aminophenol	79.2	65	-	27
Ethyl-p-aminobenzoate	82.5	38.8	71	27
2-Aminopyridine	0	---,10	34	27,28
3-Aminopyridine		33		28

a   Yields reported are taken from A. Roe, Org. Reactions, 5, 193 (1949)

It has been reported by Bergman[29-31] in a series of papers that diazonium fluoborates can be decomposed in acetone or water in the presence of cuprous chloride. The results of the fairly large number of arylfluorides prepared by this method are summarized in Table 2.

In the second paper of the series (31) yields of 52, 47, and 61% of arylfluoride are reported from the decomposition of ortho, meta, and para-nitrobenzenediazonium fluoborates, respectively. However, Barben and Suschitzky[32] in an attempt to prepare 3-fluoro-1-methyl-2-nitrobenzene from the amino precursor by Bergmann's method obtained in 75% yield o-nitrotoluene instead. They also reported that Bergmann's method failed in the decomposition of the diazonium fluoborates of o-nitrobenzene, 4-methyl-2-nitrobenzene, 2-methyl-6-nitrobenzene, 3-methyl-2-nitrobenzene, and 4-carboxybenzene. In all cases some deamination occured and some of the chloro compound was formed but none of the desired fluoride could be obtained. Again, Fisher and Joullie[33] reported that Bergmann's method failed in the

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29 E.D. Bergmann and S. Berkovic, J. Org. Chem., 26, 919 (1961).

30 E.D. Bergmann and M. Bentov, ibid., 19, 1594 (1954).

31 E.D. Bergmann, S. Berkovic, and R. Ikan, J. Am. Chem. Soc., 78, 6057 (1956).

32 I.K. Barben and H. Suschitzky, Chem. and Ind. (London), 1039 (1957).

33 E.C. Fisher and M.M. Joullie, J. Org. Chem., 23, 1944 (1958).

Table 2

Decomposition of Diazonium Fluoborates in Acetone or Water

Amine	Percent Yield of Diazonium Fluoborate	Percent Yield of Fluoroaromatic	Reference
p-Aminoacetanilide	—	82^a	30
m-Aminoacetanilide	—	75^a	30
4-Amino-4'-acetamidobiphenyl	—	62^a	30
4-Amino-4'-acetamido-3,3'-dimethoxybiphenyl	—	37^a	30
4'-Amino-2-acetamidobiphenyl	—	59^a	30
4-Fluoro-1-acetamidonaphthalene	—	69^a	30
5-Fluoro-1-acetamidonaphthalene	—	55^a	30
p-Phenylenediamine	95-98	38	31
m-Phenylenediamine	96	28	31
o-Nitroaniline	95	52	31
m-Nitroaniline	97	47	31

14

Table 2 (contd.)

Amine	Percent Yield of Diazonium Fluoborate	Percent Yield of Fluoroaromatic	Reference
p-Nitroaniline	98	61	31
o-Aminobenzoic acid	51	48	31
p-Aminobenzoic acid	50	43	31
p-Aminoacetophenone	88-90	24	31
Benzidine	90	72	31,29
p-Aminophenylacetic acid	—	87	31
p-Aminocinnamic acid	76	48	31
1-Naphthylamine	92	46	31,29
2-Naphthylamine	95	54	31,29
1-Aminoanthraquinone	88	72	31,29
2-Aminoanthraquinone	95,84	86,47	31,29
2-Aminofluorene	77	60	31
p-Aminophenol	—	71	31
o-Aminophenol	—	40	31

15

Table 2 (contd.)

Amine	Percent Yield of Diazonium Fluoborate	Percent Yield of Fluoroaromatic	Reference
p-Aminoacetanilide	65	55	31
o-Chloroaniline	—	16[a]	29
5-Chloroanthranilic acid	—	36[a]	29
p-Bromoaniline	50	30	29
o-Toluidine	81	21	29
m-Toluidine	75	21	29
p-Toluidine	82	17	29
2,3-Dimethylaniline	85	30	29
2,4-Dimethylaniline	35	17	29
2,5-Dimethylaniline	82	19	29
2-Aminobiphenyl	75	24	29
2,2'-Diamino-6,6'-dimethyl-biphenyl	75	20.5	29

a   Overall yield from the amine

preparation of 5-fluorobenzimidazole from the corresponding
diazonium fluoborate. Instead of the expected fluoro com-
pound a compound which contained chlorine was obtained.
Bergmann[34] has since stated that his method is only possible
if the starting arylamine contains no strongly polar substi-
tuent on the ring. If this is the case then one would
expect the method to fail in the case of nitroarylamines.

It is interesting to note that Hu, Yeh, and Yen[35] have
reported that the thermal decomposition of diazonium fluo-
borates can be carried out with better results in a diluent
such as sand, sodium fluoride or barium sulfate. This is
not unexpected as several diluents have been used in order
to better control decomposition of these salts.[36] However,
they also stated that the decomposition can be conducted at
room temperature in a suitable solvent if a catalyst such
as powdered copper or iron, cuprous fluoborate, or active
carbon is used. They claimed that cuprous fluoborate gave
the best results. The use of cuprous fluoborate as a cata-
lyst in the preparation of arylfluorides via the decomposi-
tion of diazonium salts in a solvent appears quite similar
to Bergmann's use of cuprous chloride.

Roe, in his article on the Schiemann Reaction in Org-
anic Reactions has included tables which list the yields

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34 E.D. Bergmann and S. Berkovic, loc. cit.

35 P.F. Hu, S.L. Yeh, and C.C. Yen, J. Chinese Chem.
Soc., 18, 158 (1951). C.A., 46, 11133 (1952).

36 A. Roe, loc. cit.

and references for the preparation of all the aromatic fluorides that were obtained via the Schiemann Procedure prior to 1947. In order to provide a convenient reference to the preparation of all the aromatic prepared via the diazonium salt since that time the following table (Table3) is provided.

Table 3

Yields of Diazonium Fluoborates and Arylfluorides

Amines Containing Halogen			
Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
4-Bromoaniline	—	54[a]	38
2,5-Dibromoaniline	65.7	58.7	39
2,6-Dibromoaniline	71.4	50.1	39
3,4-Dibromoaniline	59.8	56.6	39
2,3,5-Tribromoaniline	52.1	60.6	39
2,4,5-Tribromoaniline	57.7	46.8	39
2,4,6-Tribromoaniline	70.2	53.4	39
3,4,5-Tribromoaniline	60.2	62.6	39
2,4-Dichloroaniline	—	68.7	39
2,5-Dichloroaniline	69	68.5	39
2,6-Dichloroaniline	53.6	72.7	39
3,4-Dichloroaniline	61.2	59.8	39
3,5-Dichloroaniline	78.6	65.4	39,40

19

Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
2,3,5-Trichloroaniline	—	56.9	39
2,4,5-Trichloroaniline	60.7	56.9	39
3,4,5-Trichloroaniline	67.4	56.6	39
2-Fluoroaniline	83	51	41,42
4-Fluoroaniline	—	44	43
2,4,5-Trifluoroaniline	quant.	38-40[a]	44
2,4-Difluoroaniline	—	55	45,46
2,3,5-Trifluoroaniline	89	43[a]	47
3,5-Difluoroaniline	98	62.8[a]	48
2-Chloro-4-fluoroaniline	—	—	46
2-Fluoro-5-bromoaniline	84	8[a]	49
Amines Containing Alkyl Groups			
p-Benzylaniline	—	—	50
Aminonitrodurene		59	51
Aminonitroisodurene		49.3	51

Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
Nitromesidine	95	53.7	52
Fluoromesidine	80-100	80-90	52
Difluoromesidine	90-100	78-86	52
cis-2-Aminostilbene	ca. 65	n.d.	53
trans-2-Aminostilbene	ca. 65	n.d.	53
p-t-Butylaniline	—	n.d.	54
4-(2-chloroethyl)aniline	75	n.d.	55
o-Toluidine	—	87	56
Phenols and Ethers			
2-Aminodiphenyl ether	82	—	57
4-Amino-2,6-diethylanisole	92	69	58
p-Anisidine	—	62[a]	38
o-Anisidine	—	55.5[a] - 40[a]	38,42
2,6-Dibromo-4-aminophenol	quant.	—	59

21

Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
p-Aminophenol	65	n.d.	60
4-Chloro-2,5-diethoxyaniline	90	n.d.	61
m-Aminophenol	79	n.d.	60
2-Aminophenylbenzyl ether	87	n.d.	62
o-Trifluoromethoxyaniline	—	28.8[a]	63
m-Trifluoromethoxyaniline	—	35[a]	63
o-(1,1,2-Trifluoro-2-chloro-ethoxy)aniline	—	—	64
m-(1,1,2-Trifluoro-2-chloro-ethoxy)aniline	—	—	64
p-(1,1,2-Trifluoro-2-chloro-ethoxy)aniline	—	—	64
p-Aminodiphenyl ether	—	—	60
Esters and Acids			
5-Amino-2-chlorobenzoic acid	—	30[a]	65
6-Nitroanthranilic acid	73	n.d.	66

Table 3 (contd.)
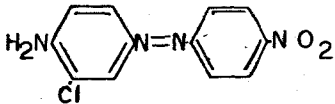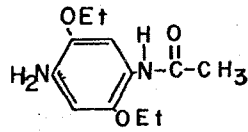
Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
Methyl anthranilate	—	46[a]	42
Methyl-2-aminoveratrate	—	—	67
p-Aminosalicylic acid methyl ester	—	31[a]	68
o-Aminobenzoic acid	51	—	69
p-Aminobenzoic acid	50	—	69
Amines, Anilides and Azo Compounds			
	—	failed	70
	quant.	n.d.	71
1-Amino-4-diethylamino-2-ethoxybenzene	90	n.d.	72
o-Amino-N-methylbenzanilide	—	n.d.	73

Table 3 (contd.)
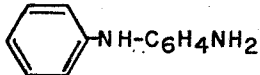
Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
3-Amino-4-fluoroacetanilide	failed	failed, 5	41,49
NH-C6H4NH2	—	failed	50
2-Amino-N-methylbenzo-1'-naphthalide	—	n.d.	74
2-Amino-N-methylbenzo-2'-naphthalide	—	n.d.	74
Ketones			
2-Aminobenzophenone	60	n.d.	75
o-Aminopropiophenone	79	n.d.	76
m-Aminopropiophenone	88	n.d.	76
2-(4'-Methylbenzoyl)aniline	56	n.d.	75
2-(4'-Methylbenzoyl)aniline	70	n.d.	75
2-(3'-Nitrobenzoyl)aniline	90	n.d.	75

Table 3 (contd.)

Amines	Yield of ArN_2BF_4	Yield of ArF	Reference
Nitro Compounds			
2,4-Dinitroaniline	92	trace	77
2-Fluoro-5-nitroaniline	—	failed	41
4-Nitroaniline	97.7, 51	48.6, 43.5[a]	70,91
3-Chloro-4-Nitroaniline	74.2	n.d.	78
2-Iodo-5-nitroaniline	92.5	44	78
1-Fluoro-2-amino-4-nitrobenzene	—	3	45
4-Chloro-3-nitroaniline	81	10	80
Naphthalene Derivatives			
1-Naphthylamine	—	57[a]	38
2,4-Dibromo-1-naphthylamine	48	62	59
2-Nitro-1-naphthylamine	—	n.d.	81
3-Nitro-2-naphthylamine	—	n.d.	81
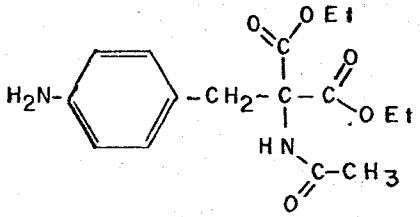
Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
Polynuclear Hydrocarbon Derivatives			
4-Aminofluorenone	98.5	67[a]	79
1-Aminofluorenone	100	78.5	79
2-NN-Dimethylamino-1-fluorenamine	80	31[a]	79
1-Aminoanthraquinone	87.5	n.d.	82
Heterocyclic Compounds			
Sulfathiazole	76	5	68
5-(p-Aminophenyl)thiazole	90	13	68
5(6) Aminobenzimidazole	86	38	83
4(7) Aminobenzimidazole	61	17	83
2-Aminoquinoline	n.i.	28[a]	84
3-Aminoquinoline	80	91.5	84
4-Aminoquinoline	—	—	84
5-Aminoquinoline	94	59	84

26

Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
6-Aminoquinoline	95.5	60	84
7-Aminoquinoline	100	27[a]	84
8-Aminoquinoline	74	33	84
1-Aminoisoquinoline	—	13[a]	84
3-Aminoisoquinoline	—	49[a]	85
4-Aminoisoquinoline	—	36[a]	85
5-Aminoisoquinoline	—	67[a]	
2-Amino-4-methylthiazole	—	5[a]	86
Compounds with more than one Amino Group			
p-Phenylenediamine	95,80	—	69,64
m-Phenylenediamine	96,54	—	69,50
2-Amino-sym-diphenylethane	50	n.d.	57
$(4\text{-}H_2NC_6H_4)_2CMeAc$	76	27[a]	87
$(p\text{-}H_2NC_6H_4)_2CH_2$	—	—	50

Table 3 (contd.)

Amine	Yield of ArN_2BF_4	Yield of ArF	Reference
Miscellaneous Compounds			
	—	50[b]	88
p-Sulfonamidoaniline	74	n.d.	89
3-(p-Aminophenyl)-DL-alanine	73	n.d.	90
3-(m-Aminophenyl)-DL-alanine	81	n.d.	90

a   Overall yield from the amine

b   Yield after hydrolysis of ester and decarboxylation to p-fluoro-β- alanine

n.i.   - not isolated

n.d.   - not decomposed by Schiemann Method

References For Table 3

38 J.D. Head and F. J. Lowes, U.S. Pat., 2,606,183. C.A., 47, P3875 (1953).

39 A. Pavlath and G. Olah, Acta. Chim. Acad. Sci. Hung., 10, 227 (1956). C.A., 51, 8666 (1957).

40 J.M. Denham and R.K. Ingham, J. Org. Chem., 23, 1298 (1958).

41 A.F. Helin and C.A. VanderWerf, J. Am. Chem. Soc., 73, 5884 (1951).

42 J.T. Minor and C.A. VanderWerf, J. Org. Chem., 17, 1425 (1952).

43 S.G. Malkevich and L.V. Chereshkevich, Plasticheskii Massy, 4, 1 (1960). C. A., 55, 421 (1961).

44 G.C. Finger, F.H. Reed, D.M. Burners, D.M. Fort, and R.R. Blough, J. Am. Chem. Soc., 73, 145 (1951).

45 F. Weygand, R. Lowenfeld, and E.F. Moller, Ber., 84, 101 (1951).

46 G.C. Finger and R.E. Oesterling, J. Am. Chem. Soc., 78, 2593 (1956).

47 G.C. Finger, F.H. Reed, and R.E. Oesterling, J. Am. Chem. Soc., 73, 152 (1951).

48 G.C. Finger, F.H. Reed, and J.L. Finnerty, J. Am. Chem. Soc., 73, 153 (1951).

49 A. Roe, W.A. Yarnall, and V.A. Hoyle Jr., J. Org. Chem., 21, 28 (1956).

50 J. Lichtenberger and R. Thermet, Bull. soc. chim. France, 318 (1951). C. A. 46, 3509 (1952).

51 G. Grassini, G. Illuminati, and G. Marino, Gazz. Chim. ital., 86, 1138 (1956). C. A. 52, 1937 (1958).

52 G.C. Finger, F.H. Reed, E.W. Maynert, and A.M. Weiner, J. Am. Chem. Soc., 73, 149 (1951).

53 D.F. Detar and Yun-Wen Chu, J. Am. Chem. Soc., 76, 1686 (1954).

54 G.M. Kosolapoff, J. Am. Chem. Soc., 76, 3222 (1954).

55 R.H. Wiley and W.A. Trinler, J. Poly. Sci., 42, 113 (1960).

56 M. Hudlicky, Collection Czech. Chem. Communs., 25, 1199 (1960). C.A., 55, 1502 (1961).

57 D.F. DeTar and T.E. Whitely, J. Am. Chem. Soc., 79, 2498 (1957).

58 S. Hunig, H. Balli, H. Nother, and H. Geiger, Ann., 628, 75 (1959).

59 U. Wannagat and G. Hohlstein, Ber., 88, 1839 (1955).

60 E.S. Lewis and M.D. Johnson, J. Am. Chem. Soc., 81, 2070 (1959).

61 K.H. Klassens and C.J. Schoot, Rec. trav. chim., 72, 91 (1953).

62 L.D. Freedman, G.O. Doak, and L. Petit, J. Org. Chem., 25, 140 (1960).

63 L.M. Yagupol'skii and V.I. Troitskaya, Zhur. Obshchei Khim., 31, 915 (1961). C.A., 55, 23409 (1961).

64 J. Lichtenberger and A.M. Geyer, Bull. soc. chim. France, 820 (1957).

65 E.D. Bergmann and S. Berkovic, J. Org. Chem., 26, 919 (1961).

66 L.D. Freedman and G.O. Doak, J. Org. Chem., 26, 2082 (1961).

67 C. Kaiser and A. Burger, J. Am. Chem. Soc., 79, 4365 (1957).

68 F. Zuber, E. Sorkin, and H. Erlenmeyer, Helv. Chim. Acta., 33, 1269 (1950).

69 E.D. Bergmann, S. Berkovic, and R. Ikan, J. Am. Chem. Soc., 78, 6037 (1956).

70 O. Neunhoeffer and W. Rushe, Ann., 610, 143 (1957).

71 K.H. Klassens and C.J. Schoot, Rec. trav. chim., 72, 178 (1953).

72 K.H. Klassens and C.J. Schoot, Rec. trav. chim., 71, 1086 (1952).

73 R.A. Heacock and D.H. Hey, J. Chem. Soc., 1508 (1952).

74 D.H. Hey and D.G. Turpin, J. Chem. Soc., 2471 (1954).

75 D.F. DeTar and D.I. Relyea, J. Am. Chem. Soc., 76, 1680 (1954).

76 B.L. Zenitz and W.H. Hartung, J. Org. Chem., 11, 444 (1946).

77 J.C. Brunton and H. Suschitzky, J. Chem. Soc., 1035 (1955).

78 R.W. Bost and L.D. Quin, J. Org. Chem., 18, 358 (1953).

79 T.L. Fletcher, M.J. Namkung, Hsi-Lung Pan, and W.H. Wetzel, J. Org. Chem., 25, 996 (1960).

80 R.L. Heppolette and J. Miller, J. Am. Chem. Soc., 75, 4265 (1953).

81 D.N. Brown, D.H. Hey, and C.W. Rees, J. Chem. Soc., 3873 (1961).

82 A.M. Lakin and G.S. Petrova, Zhur. Obshchei Khim., 27, 2171 (1957). C.A., 52, 6297 (1958).

83 E.C. Fisher and M.M. Joullie, J. Org. Chem., 23, 1944 (1958).

84 A. Roe and G.F. Hawkins, J. Am. Chem. Soc., 71, 1785 (1949).

85 A. Roe and C.E. Teague Jr., J. Am. Chem. Soc., 73, 687 (1951).

86 R.D. Beaty and W.K.R. Musgrave, J. Am. Chem. Soc., 875 (1952).

87 M.E. Wolff and F.F. Owings, J. Org. Chem., 25, 1235 (1960).

88 T. Okuda and S. Tatsumi, J. Biochem. (Tokyo), 44, 631 (1957). C.A., 52, 5293 (1958).

89 R.D. Englert and O.J. Sweeting, J. Am. Chem. Soc., 70, 2977 (1948).

90 H.F. Gram, C.W. Mosher, and B.R. Baker, J. Am. Chem. Soc., 81, 3103 (1959).

91 G.B. Bachman and T. Hokama, J. Am. Chem. Soc., 79, 4370 (1957).

2. The Replacement of an Aromatic Amino Group with a Hydrogen Atom.

Several methods are known for the replacement of a primary aromatic amino group with a hydrogen atom by reduction of its intermediate diazonium compound. The more generally used of these procedures involve the use of ethanol,[92] hypophosphorous acid,[93] or alkaline formaldehyde[94] as the reducing agents. Sodium stannite,[95] stannous chloride and sodium sulfite[96] have also been used but only in a limited number of cases. The ethanol procedure involves diazotization of the amine most commonly in sulfuric acid and the addition of the diazonium sulfate to hot ethanol. As an alternative the diazotization may be carried out in ethanol and the reaction mixture held at reflux temperature until no more gas is evolved.[97] The isolation of the product is determined by its own properties and hence depends on the specific compound involved. In the hypophosphorous acid method the amine is diazotized in a cold solution of hydrochloric acid. A large excess of a cold solution of

92 P. Griess, Phil. Trans. Roy. Soc. (London), A154, 683 (1864).

93 J. Mai, Ber., 35, 163 (1902).

94 R.Q. Brewster and J.A. Poje, J. Am. Chem. Soc., 61, 2418 (1939).

95 P. Friedlander, Ber., 22, 587 (1889).

96 A. Haller, Ber., 18, 90 (1885).

97 G.H. Coleman and W.F. Talbot, in Organic Synthesis, (New York, 1943), Coll. Vol. 2, p. 592.

hypophosphorous acid is added with stirring to the diazo-
nium chloride. The cold mixture is stirred for an additio-
nal hour and finally placed in a refrigerator for 24 hours.
The product is then isolated in a suitable manner. The
alkaline formaldehyde procedure also involves the decomp-
osition of a diazonium chloride. Here the solution of the
diazonium chloride is poured into an aqueous solution of
formalin and sodium hydroxide. Nitrogen is evolved and the
product separated according to its own nature. These pro-
cedures are discussed in more detail by Kornblum[98] in Organic
Reactions.

Several modifications of these standard methods have
been developed which give increased yields of the reduced
product. Roe and Graham[99] obtained better results with the
ethanol deamination procedure through the use of diazonium
fluoborates rather than the usual chlorides or sulfates and
by carrying out the reduction in the presence of zinc. This
procedure was much more successful than the usual ethanolic
deamination method in the preparation of benzene from ani-
line and toluene from any one of the three isomeric methyl-
anilines. A yield of 46.5% of benzene was obtained from
benzenediazonium fluoborate and toluene was prepared in
yields of 82.2, 73.7, and 84.8% from the diazonium fluobor-

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98 N. Kornblum, in Organic Reactions, (New York, 1944),
Vol. 2, p. 262.

99 A. Roe and J.R. Graham, J. Am. Chem. Soc., 74, 6297
(1952).

ates derived from ortho, meta, and para-toluidine, respectively. These results are in contrast to a yield of only 5% in the preparation of benzene from aniline by the usual procedure. In the deamination of the diazonium salts derived from ortho, meta, and para-toluidine via the ethanol method ether formation, which is always a problem in this procedure becomes predominant and only the corresponding methylphenetoles are isolated. The modified ethanol deamination method has also been extended to the reduction of some heterocyclic amines. For example, the above authors have obtained quinoline in 34% yield by the reduction of quinoline-6-diazonium fluoborate and pyridine in 26.3% yield from the reduction of pyridine-3-diazonium fluoborate.

An interesting modification of the hypophosphorous acid-cuprous oxide deamination procedure enabled Finger and White[100] to reduce a nitro substituent to an amino group while reduction of the diazo group was carried out. Usually in hypophosphorous acid-cuprous oxide reductions of diazonium salts the cuprous oxide is thought of as a catalyst and hence a small and arbitrary quantity is added to the reaction mixture. The above authors, however, discovered that a nitro group could be simultaneously reduced during hypophosphorous acid deaminations if a three fold excess of cuprous oxide was used and if the reaction mixture was heated at 90-100° on a steam bath for four hours. Through the

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100 G.C. Finger and R.H. White, J. Org. Chem., 23, 1612 (1958).

use of this method they were able to prepare 3,5-difluoro-4-chloroaniline from 4,6-difluoro-5-chloro-2-nitroaniline. Similarly 4-fluoroaniline and 3,5-dichloroaniline were prepared from the corresponding nitroamines in yields of 55 and 59%, respectively.

Kornblum and Iffland[101] have shown that it is possible to reduce an aromatic amino group in the presence of an aliphatic amino group by conducting the diazotization at a pH less than three. These authors used hypophosphorous acid both to set the proper pH for the diazotization and to reduce the diazonium salts obtained. The overall reaction scheme is shown in Figure 3. The selective deamination of
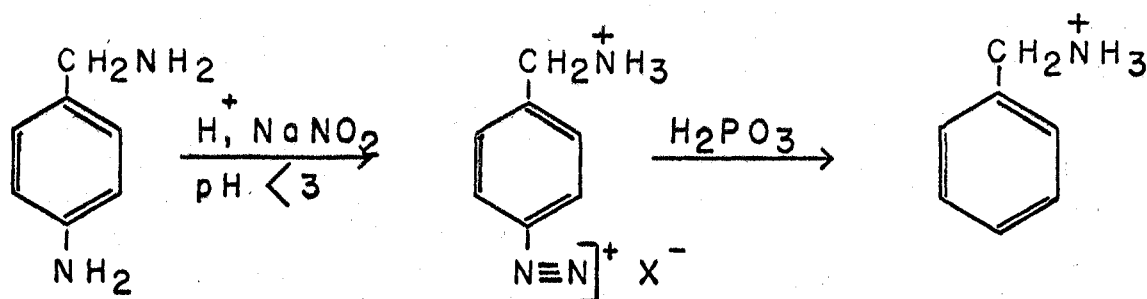

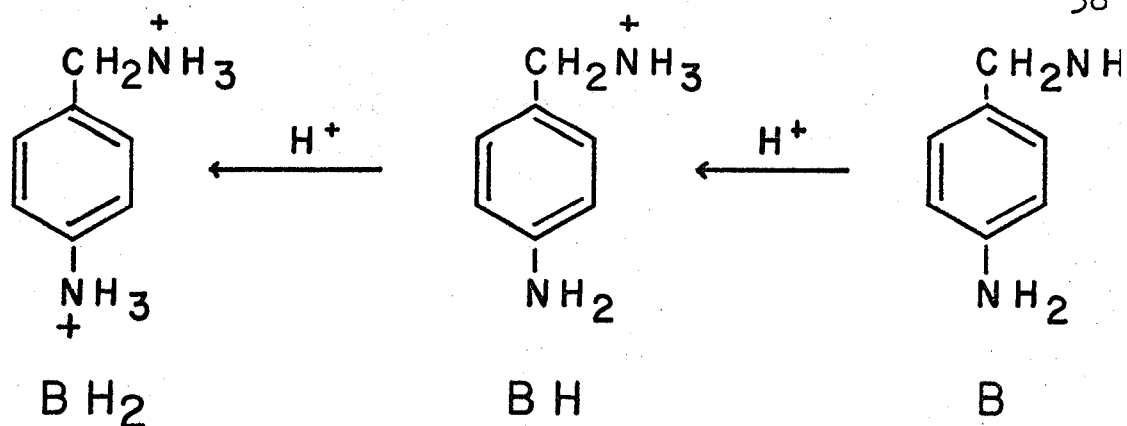Fig. 3. The selective deamination of an aromatic amino group.

m-aminobenzylamine, p-aminobenzylamine, 2-(o-aminophenyl)-ethylamine, 2-(m-aminophenyl)ethylamine, and 2-(p-amino-phenyl)ethylamine gave the corresponding aliphatic mono-amines in yields of 87, 84, 52, 70, and 71%, respectively.

101 N. Kornblum and D.C. Iffland, J. Am. Chem. Soc., 71, 2137 (1949).

Several other diamines were treated in the same manner and in all cases the aromatic amino group was replaced by a hydrogen atom and a good yield of the aliphatic amine was obtained. Hughes, Ingold, and Ridd[102] have shown in a series of papers that diazotization takes place by attack of the nitrosating agent on the free amino group and not on the protonated form of the amine. This fact offers an explanation for the observation that an aromatic amino group may be diazotized without affecting an aliphatic amino group since it would be expected that the aliphatic group would be protonated more readily than the aromatic group. Indeed Gillis[103] calculated the relative amounts of each of the three species derived from p-aminobenzylamine that would be present at various pH values based on the assumption that the dissociation constant for the aliphatic amino group is of the same order of magnitude as that of benzylamine and that the dissociation constant for the aromatic amino group is of the same order of magnitude as that of p-toluidine. These calculations (see Figure 4) show that no appreciable proportion of free aliphatic amino groups is present at a pH less than three. Since there is such a small proportion of free aliphatic group present it cannot be diazotized while at the same pH the aromatic amino group remains to a great extent in the free form and hence is

102 E.D. Hughes, C.K. Ingold, and J.H. Ridd, J. Chem. Soc., 58 (1958) and following papers.

103 R.B. Gillis, J. Chem. Educ., 31, 344 (1954).

$$CH_2\overset{+}{N}H_3 \quad\xleftarrow{\ H^+\ }\quad CH_2\overset{+}{N}H_3 \quad\xleftarrow{\ H^+\ }\quad CH_2NH$$

$$\underset{+}{\overset{+}{N}H_3} \qquad\qquad NH_2 \qquad\qquad NH_2$$

$$B\,H_2 \qquad\qquad\qquad B\,H \qquad\qquad\qquad B$$

pH	1	2	3	4
B	1	100	6,700	167,000
BH	2,380,000	22,790,000	159,520,000	398,700,000
BH2	476,190,000	455,780,000	319,040,000	79,700,000

Fig. 4. The relative amounts of each protonated form of p-aminobenzylamine at various pH levels.

susceptible to attack by the nitrosating agent.

Several methods have been reported for the reduction of diazonium salts in non-aqueous media. The first of these was reported in a German Patent by Zerweek, Schubert, and Fleischhauer.[104] They found that the diazotization of aromatic amines with N oxides, nitrosyl chloride, or butyl nitrite in the presence of a salt, ester, or amide of formic acid led to replacement of the diazo group by a hydrogen atom. Thus, diazotization of 2,5-dichloroaniline with butyl nitrite in dimethylformamide produced p-dichlorobenzene.

Another non-aqueous reduction of aromatic amines was

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104 W. Zerweek, M. Schubert, and R. Fleischhauer, Ger. Pat., 901,175. C.A., 50, P12111 (1956).

recently reported by Hendrickson.[105] His method involves
the diazotization of the amine and the formation of the
diazonium fluoborate. The diazonium fluoborate is then
isolated and dried prior to its reduction with sodium boro-
hydride in either cold tetrahydrofuran or methanol. The
method appears to be simple to carry out and good yields of
reduced product were obtained in the examples he reported.
Nitro and carboxylic acid substituents were not simultan-
eously reduced by the sodium borohydride and therefore the
method appears to have many advantages. However, only a
very few examples were given and further work will be re-
quired before the actual scope and limitations of this
reaction are known.

Meerwein[106] has reported the use of dioxane, dioxolane,
diglyme, and tetrahydrofuran as hydride transfer agents in
the reduction of aryldiazonium chlorides. The yield of
reduction product in each case with the limited number of
examples chosen was good. The authors' attempts to reduce
diazonium fluoborates in tertiary amines apparently did not
show promise even though p-chlorobenzenediazonium fluoborate
and 2,4,6-trichlorobenzenediazonium fluoborate gave yields
of 45% and 65%, respectively, of reduction product. In

105 J.B. Hendrickson, J. Am. Chem. Soc., 83, 1251
(1961).

106 H. Meerwein, H. Allendorfer, P. Beckmann, F. Kun-
nert, H. Morschel, F. Pawellek, and K. Wunderlich, Angew.
Chem., 70, 211 (1958).

more recent work on diazonium fluoborates Meerwein[107] has

shown that 4-trimethylammonium-2,6-dichlorobenzenediazonium

chloride fluoborate, which is formed by the reaction of

trimethylamine with 2,4,6-trichlorobenzenediazonium fluo-

borate in acetonitrile (see Figure 5) may be reduced to

1,3,5-trichlorobenzene by the action of 1,3 dioxolane.
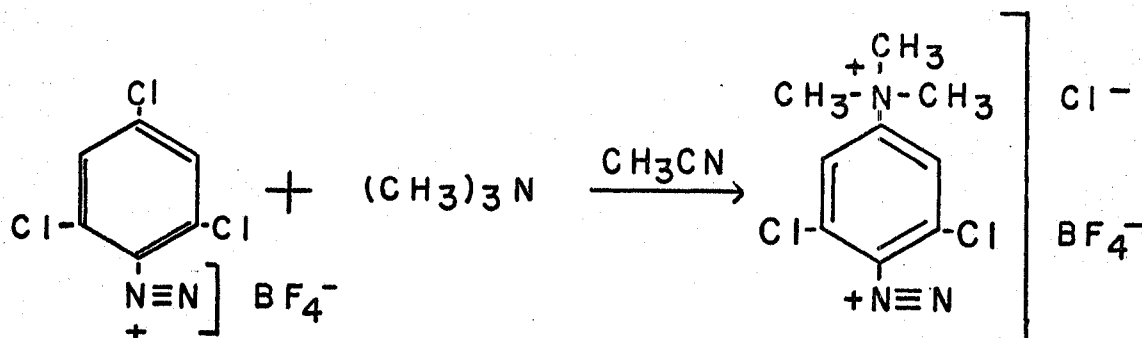
Fig. 5. The preparation of 4-trimethylammonium-2,6-
dichlorobenzenediazonium fluoborate chloride.

Since Meerwein was primarily interested in the mech-
anism of ionic hydrogenation and dehydrogenation and in
ionic transfer mechanisms he has done little work to extend
this method as a general reaction. However, from the lim-
ited number of compounds with which he has worked it appears
as though the reaction has good possibilities as a general
deamination procedure.

107 H. Meerwein, K. Wunderlich, and K.F. Jenner, Angew.
Chem., 74, 807 (1962).

DISCUSSION OF EXPERIMENTAL RESULTS.

1. The Preparation of Arylfluorides.

The literature of Organic Chemistry contains a great number of references with respect to the study of reactions and their use. A modification or an innovation which can broaden the scope of an organic reaction is of fundamental significance since the route to new compounds which might have biological or industrial importance may be realized as a result. Workers are continually trying to find new reactions and to improve existing ones. In this latter respect the Schiemann Reaction is no exception. Indeed, interest in the past fifteen years in fluorine containing compounds in general has been manifested in the literature by the appearance of several papers dealing with the uses and modifications of this useful reaction.

Our interest in the Schiemann Reaction stemmed from the observation that of several cases reported in the literature the yields of the Schiemann Reaction are low because of the relatively high solubility of some diazonium fluoborates. This is particularly glaring with aromatic amino acids. Thus the yield of diazonium fluoborate obtained from ortho and para-aminobenzoic acids are 0-46 and 76-84%,

41

respectively.[1] It is reasonable to expect that a method which results in the precipitation of a larger amount of some intermediate diazonium salt will give greater yields overall of the fluoroaromatic if the decomposition of the salt proceeds as well as it does in the normal Schiemann Reaction. Accordingly, the possibility of using hexafluorophosphoric acid instead of fluoboric acid to precipitate the diazonium salts for use in the preparation of arylfluorides was investigated. The overall reaction sequence is shown in Figure 6.
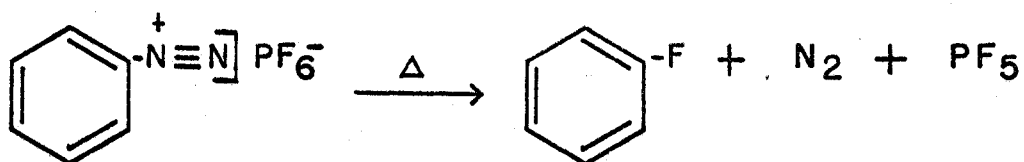
Fig. 6. The preparation of arylfluorides via the diazonium hexafluorophosphate method.

It was expected that diazonium hexafluorophosphates should be less soluble in aqueous solutions than the corresponding fluoborates because of their larger size. It has been shown that the larger the anion in the diazonium salt the more insoluble the salt will be if other factors

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1 A. Roe, in Organic Reactions, (New York, 1949), Vol. 5, p.193.

are approximately equal.[2] In addition to the increased
yields of intermediate salt that would be expected by the
use of the hexafluorophosphate anion one would also expect
that its thermal decomposition would give greater yields
than with the diazonium fluoborate. Thermal decomposition
of aryldiazonium hexafluorophosphates yields phosphorous
pentafluoride which is a weaker Lewis acid than the boron
trifluoride that is produced in the normal Schiemann
Reaction. Therefore the use of the hexafluorophosphate
salt should minimize any undesirable side reactions and
lead to a greater yield of arylfluoride.

The first report of the preparation and decomposition
of aryldiazonium hexafluorophosphates in the literature is
that of Lange and Mueller[3] in 1930. They obtained a low
yield of 4,4'-difluorobiphenyl and an unstated yield of
fluorobenzene via the thermal decomposition of the corres-
ponding diazonium hexafluorophosphates. This reaction was
given no further consideration in the literature until the
report by Newman and Galt[4] of the conversion of 6-bromo-2-
naphthylamine and 1-bromo-3-naphthylamine to the fluoro-
analogs via the diazonium hexafluorophosphate method.

In general, the hexafluorophosphate method is a con-

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2 H.F. Halliwell and S.C. Nyberg, J. Chem. Soc., 4603
(1960).

3 W. Lange and E. Mueller, Ber., 63, 1058 (1930).

4 M.S. Newman and R.H.B. Galt, J. Org. Chem., 25, 214
(1960).

venient procedure for the preparation of arylfluorides. A polypropylene (Nalgene) graduated cylinder was used to measure the hexafluorophosphoric acid solution and rubber gloves were used to protect the hands but it was not found necessary to use copper or monel ware for either the preparation or decomposition of the diazonium hexafluorophosphates. Since the aqueous solution of hexafluorophosphoric acid does contain a small amount of free hydrofluoric acid the glassware used for the preparation and decomposition of the diazonium hexafluorophosphates did become etched. However, a large number of preparations could be carried out in the same equipment before the glass was seriously weakened by etching. Contamination of the diazonium salt by dissolved silicates from the glassware does not appear to have any appreciable effect on the yield of arylfluoride produced during the decomposition. The only equipment beyond the usual laboratory glassware that is required for the reaction is an efficient fume hood which is capable of removing the large volume of phosphorous pentafluoride that is produced during the decomposition of the diazonium salt. The simplicity of the equipment that is required for this reaction is in marked contrast to that required for the use of anhydrous hydrofluoric acid in the diazonium fluoride method.

In contrast to most other diazonium salts none of the diazonium hexafluorophosphates that were prepared in this laboratory showed any evidence of explosion hazard. M. Paul-

schock and B.C. McKusick, the checkers on a submission to
Organic Synthesis for the preparation of 1-bromo-2-fluoro-
benzene[5] examined o-bromobenzenediazonium hexafluorophosphate
in laboratories of the Dupont Co. Explosives Department.
They found it to be sensitive to neither shock nor static
electricity and to decompose rapidly but not detonate when
heated to 250°. Thus these salts may be handled readily
with no danger. However, they should be isolated from heat,
particularly when in closed containers, since slow decompo-
sition liberates nitrogen and phosphorous pentafluoride
which build up a considerable pressure and could conceivably
fracture a container. In addition open samples should pro-
bably be kept in a fume hood in order to avoid contamination
of the laboratory with small quantities of phosphorous
pentafluoride gas from the slow decomposition of the salt
even at room temperature.

It has been found that in almost all cases the yield
of aryldiazonium hexafluorophosphate by our method was
quantitative or very nearly so. With the exception of p-
carboxybenzenediazonium hexafluorophosphate all the salts
could be liberally washed with cold water without any
appreciable loss. Hence any coprecipitated sodium chloride
could be removed from the diazonium compound before thermal
decomposition. Any organic impurities were removed by
washing with a solution of eighty parts ether and twenty

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5 K.G. Rutherford and W. Redmond, in Organic Reactions,
(New York, 1963), Vol. 43, p.12.

parts methanol. In addition to the removal of organic impurities this washing also facilitated drying of the salt.

In general the decomposition points of the diazonium hexafluorophosphates investigated were sharp and were slightly higher than those reported for the diazonium fluoborates. A comparison of the decomposition points of the corresponding diazonium salts can be seen in Table 4.

In most cases the thermal decomposition of the aryldiazonium hexafluorophosphates was smooth and easily controlled. However, a more violent reaction was noted when o-nitrobenzenediazonium hexafluorophosphate was heated and considerable charring of the reaction mixture occured. This is also noted in the decomposition of the corresponding fluoborate and in both cases the yield of o-fluoronitrobenzene is low.

It is generally preferable to decompose the diazonium hexafluorophosphate in a diluent such as mineral oil in those cases in which the arylfluoride can be readily isolated by distillation with steam. This technique gives better control over the temperature of the decomposition than does the application of direct heat to the salt in the absence of a diluent. Slightly improved yields were also obtained when the decomposition of the diazonium hexafluorophosphate was effected at the greatest possible rate. Care must be exercised, however, that the reaction does not become too violent under these conditions.

Some increase in yield of arylfluoride was noted in

nearly every case through the substitution of hexafluoro-
phosphoric acid for fluoboric acid in the Schiemann Reaction.
Although in some cases no appreciable advantage in the use of
the hexafluorophosphate salt was noted, several amines were
converted in greatly increased yields to their fluoro ana-
logs. Outstanding in this respect are the increased yields
of o-fluorobenzoic acid, p-fluorobenzoic acid, o-fluoro-
bromobenzene, p-fluoroanisole, and p-fluorophenol. Increa-
ses in yields of the above compounds were 52, 49, 35, 27,
23, and about 15% respectively. A comparison of the yields
obtained by the two methods can be seen in Table 4.

Table 4

Hexafluorophosphoric Acid versus Fluoboric Acid in the Schiemann Reaction

Aromatic Amine	Fluoboric Acid Method[a]			Hexafluorophosphoric Acid Method		
	% Yield of ArN_2BF_4	Decomp. Temp.	% Yield of ArF	% Yield of ArN_2PF_6	Decomp. Temp.	% Yield of ArF
o-Aminobenzoic acid	0-46	125	19(9)[b]	79	129	78(61)
p-Aminobenzoic acid	76-84	-	Failed	77	150	64(49)
o-Bromoaniline	50	156	81(40)	97	156	77(75)
p-Bromoaniline	64	133	75(52)	Quant.	144	(79)
p-Aminophenol	Failed	-	——	77	120-130	10-20
p-Chloroaniline	90	-	Not attempted	97	137	75(73)
o-Aminoanisole	52-91	125	54-67	Quant.	120	(60)
p-Aminoanisole	85	139	67(47)	Quant.	149	(70)

48

Table 4 (contd.)

Aromatic Amine	Fluoboric Acid Method			Hexafluorophosphoric Acid Method		
	% Yield of ArN_2BF_4	Decomp. Temp.	% Yield of ArF	% Yield of ArN_2PF_6	Decomp. Temp.	% Yield of ArF
o-Nitroaniline	63-92	133	10-19	97	161	10-20
m-Nitroaniline	79-99	170-178	43-54	Quant.	-	(58)
p-Nitroaniline	80-100	156	40-58	Quant.	170	(63)
o-Aminotoluene	59-90	106	90	97	110	60(58)
m-Aminotoluene	79-90	108	(87)	Quant.	110	(57)
p-Aminotoluene	67-90	110	(70)	97	112	(71)
2-Aminopyridine	Not isolated	0	(34)	Not isolated	-10	(33)

a   Data from A. Roe, loc. cit.

b   Numbers in parentheses represent over-all yields.

2. The Reduction of Diazonium Hexafluorophosphates in Tetra-
methylurea.

A diazonium fluoborate which reacts too violently when
heated by itself may decompose quite smoothly in the
presence of a diluent. Hence, improved yields of fluoro-
aromatic are often obtained via the Schiemann Reaction when
the intermediate salt is thermally decomposed in a diluent.
Accordingly, heavy mineral oil and xylene were tried for
this purpose in an attempt to increase the yields obtained
via the hexafluorophosphate method. However, it was consi-
dered likely that decomposition would occur at a lower
temperature and would be even more readily controlled if a
suitable solvent could be found for these salts. Attempts
to use tetrahydrofuran and dimethylformamide as media for
the decomposition met with little success. In an effort to
find a better solvent the diazonium hexafluorophosphate
derived from anthranilic acid was added to tetramethylurea.
Immediate evolution of a gas was noted and the temperature
of the reaction mixture rose. After the evolution of
nitrogen had ceased the reaction mixture was poured over an
ice-hydrochloric acid mixture and a red precipitate formed.
Treatment with Norit and recrystallization from a chloro-
form-petroleum ether (b.p. 30-60°) solvent pair gave a
colourless precipitate which on further examination proved
to be benzoic acid. Thus the diazonium salt was reduced
and little or no o-fluorobenzoic acid was formed. A yield
of 80-85% of reduced product was obtained in several runs

in marked contrast to the yields obtained by reductions
with ethanol (ethyl benzoate, 53%) and with alkaline form-
aldehyde (benzoic acid, 25%). Because of the greatly in-
creased yield of benzoic acid that was obtained by this
procedure several other diazonium hexafluorophosphates were
similarly treated in an effort to ascertain the scope of
the reaction

All of the aryldiazonium hexafluorophosphates conven-
iently decomposed spontaneously and exothermally in tetra-
methylurea. Decomposition was slow with some of the salts
unless the reaction mixture was warmed to about 50° at which
temperature a much more rapid evolution of nitrogen began.

Reduction of diazonium hexafluorophosphates with
tetramethylurea shows many points in common with reductions
of diazonium salts with ethanol. In both cases very good
yields of reduction product are obtained when electron with-
drawing groups are present on the aromatic nucleus. Poor
yields of reduction product are obtained by both methods
when they are applied to the reduction of diazonium salts
derived from amines which contain electron donating groups.
In these cases the hypophosphorous acid and alkaline form-
aldehyde procedures show a distinct advantage over the other
methods. In fact, the hypophosphorous acid method appears
to be the most widely applicable of these methods and to be
quite independent of other substituents on the aromatic
nucleus of the parent amine. A comparison of the tetra-
methylurea method with the more commonly used deamination

procedures can be seen in Table 5.

The mechanism of reduction by tetramethylurea is still a matter of speculation. It could quite easily be either a free radical or an ionic reaction. However, an ionic reaction pathway appears more likely in view of the work of Meerwein[6] and DeTar[7]. Meerwein has obtained very good evidence of hydride transfer in the reaction of 2,4,6-trichlorobenzenediazonium fluoborate with 2-phenyl-1,3-dioxolane to give a 55% yield of trichlorobenzene and an 80% yield of 2-phenyl-1,3-dioxolenium fluoborate.
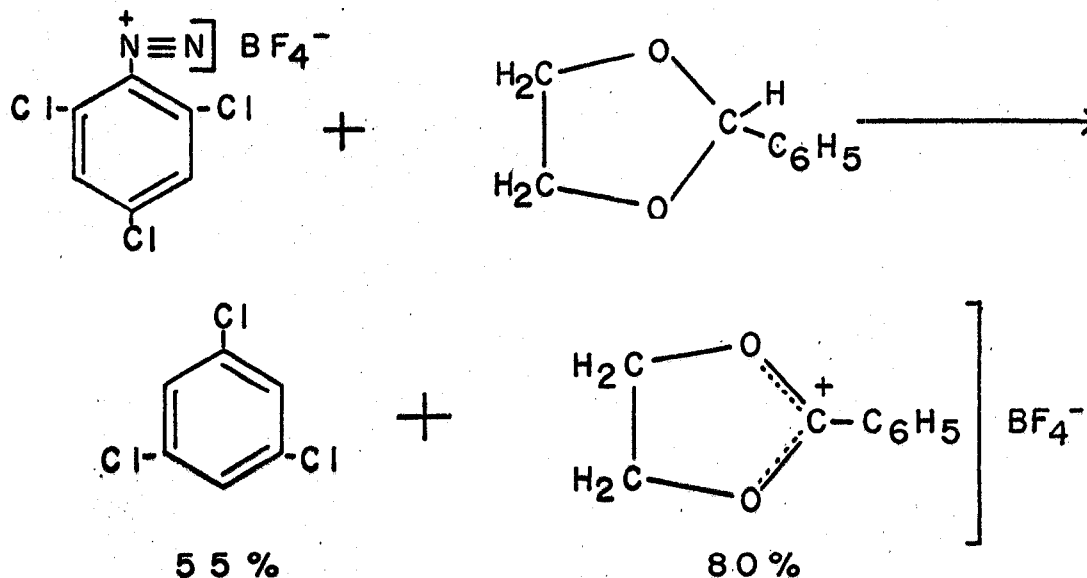

Fig. 7. The reaction of 2,4,6-trichlorobenzenediazonium fluoborate with 2-phenyl-1,3-dioxolane.

6 H.Meerwein, H. Allendorfer, P. Beckmann, Fr. Kunnert, H. Morschel, F. Pawellek, and Kl. Wunderlich, Angew. Chem., 70, 211 (1958).

7 D.F. DeTar and T. Kosuge, J. Am. Chem. Soc., 80, 6072 (1958).

Table 5

Comparison of Yield of Reduction Product via Common Procedures

Amine	Ethanol	Hypophosphorous Acid	Alkaline Formaldehyde	Tetramethyl- urea
Aniline	5	60	60	25-30
o-Toluidine	o-Methylphenetole,ca.50	70-75	80	
p-Toluidine	o-Methylphenetole,ca.50	77-83	80	25-30
o-Anisidine	Amount unstated		75	33
Anthranilic acid	Ethyl benzoate,53		25	80-85
p-Aminobenzoic acid	p-Ethoxybenzoic acid,50 + ethyl benzoate			82
o-Nitroaniline	82	75-80	20	75
p-Nitroaniline	70	55-60	10	62
p-Chloroaniline	87		50	70
o-Bromoaniline	72-80			80
p-Bromoaniline	68-80			72
p-Aminoacetophenone				43

a   Unless otherwise specified, the amino group has been replaced by hydrogen.

b   Data taken from Nathan Kornblum, Org. Reactions, 2, 262 (1944)

53

More recently Meerwein[8] has reported the reaction of triphenylmethyl fluoborate with various 1,3-dioxolanes to produce triphenylmethane and 1,3-dioxolenium fluoborate in good yields. These reactions would almost certainly be ionic in mechanism and because of their similarity to the reduction of the diazonium fluoborate may be taken as supporting evidence for the hydride transfer mechanism.

Finally he has reported that the reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate, chloride with 1,3-dioxolane gave a yield of 82% of 1,3,5-trichlorobenzene.[9] On the other hand if the reduction was carried out with 2-methyl-1,3-dioxolane in the presence of copper bronze a mixture which consisted mainly of trimethyl-3,5-dichlorophenylammonium fluoborate was obtained. The 2-methyl-1,3-dioxolane was converted to 2-chloroethyl acetate in this reaction. It is apparent from this reaction that if conditions are set to favour a free radical mechanism over an ionic one products which differ from those formed in the normal reduction reaction are isolated. The following reaction sequences were given by Meerwein to explain how the products were obtained.

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8 H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, _Ann._, _635_, 3 (1960).

9 H. Meerwein, K. Wunderlich, and K.F. Jenner, _Angew._, _Chem._, 74, 807 (1962).
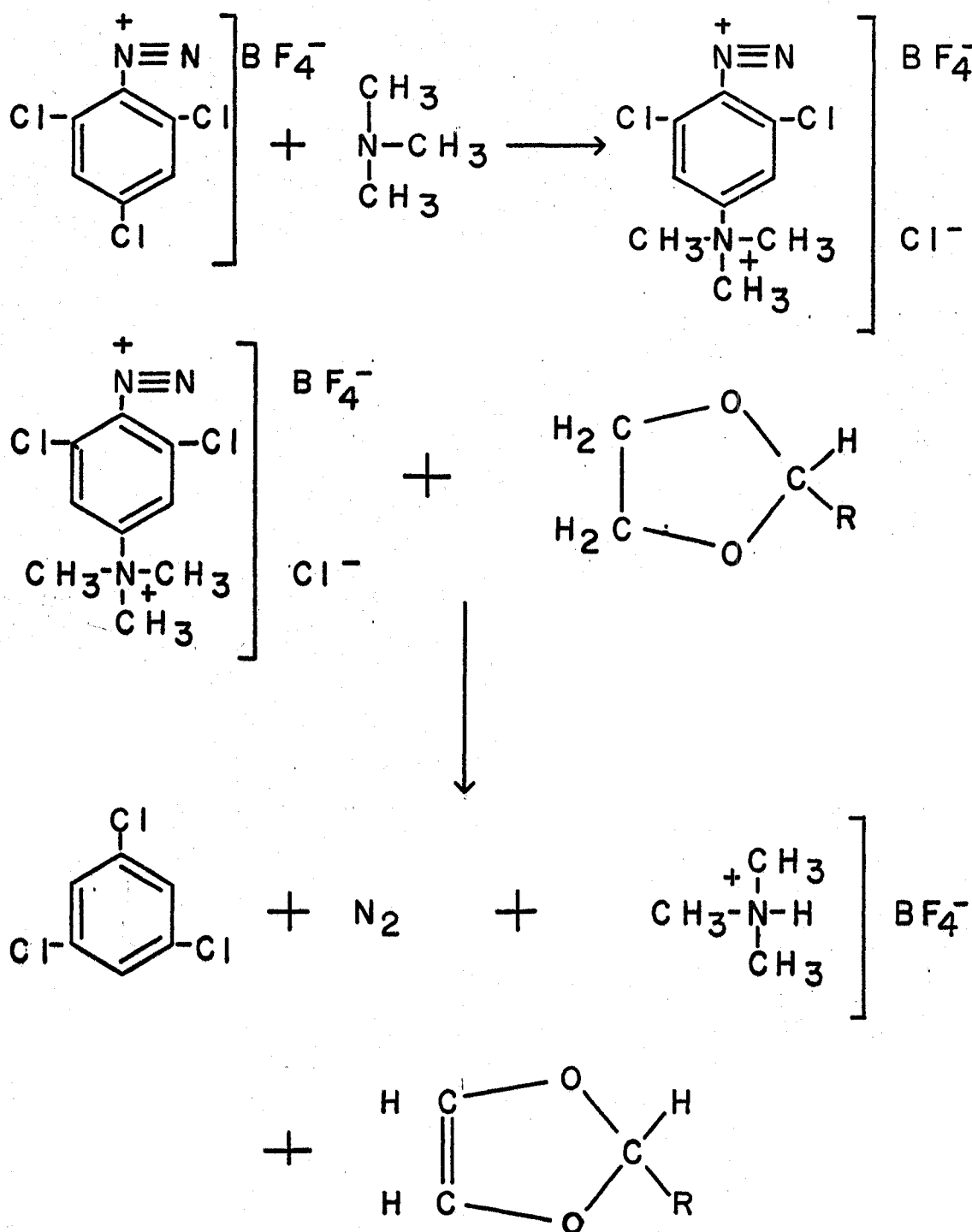
Fig. 8. The reduction of 4-trimethylammonium-2,6-di-
chlorobenzenediazonium fluoborate chloride with sub-
stituted dioxolanes.

In the above reaction sequence an ionic mechanism is in force. Both a hydride ion and a proton are lost from the substituted 1,3-dioxolane in order to reduce the diazo-compound and form trichlorobenzene.

When copper bronze is added to the reaction in order to encourage free radical reduction the following sequence occurs.
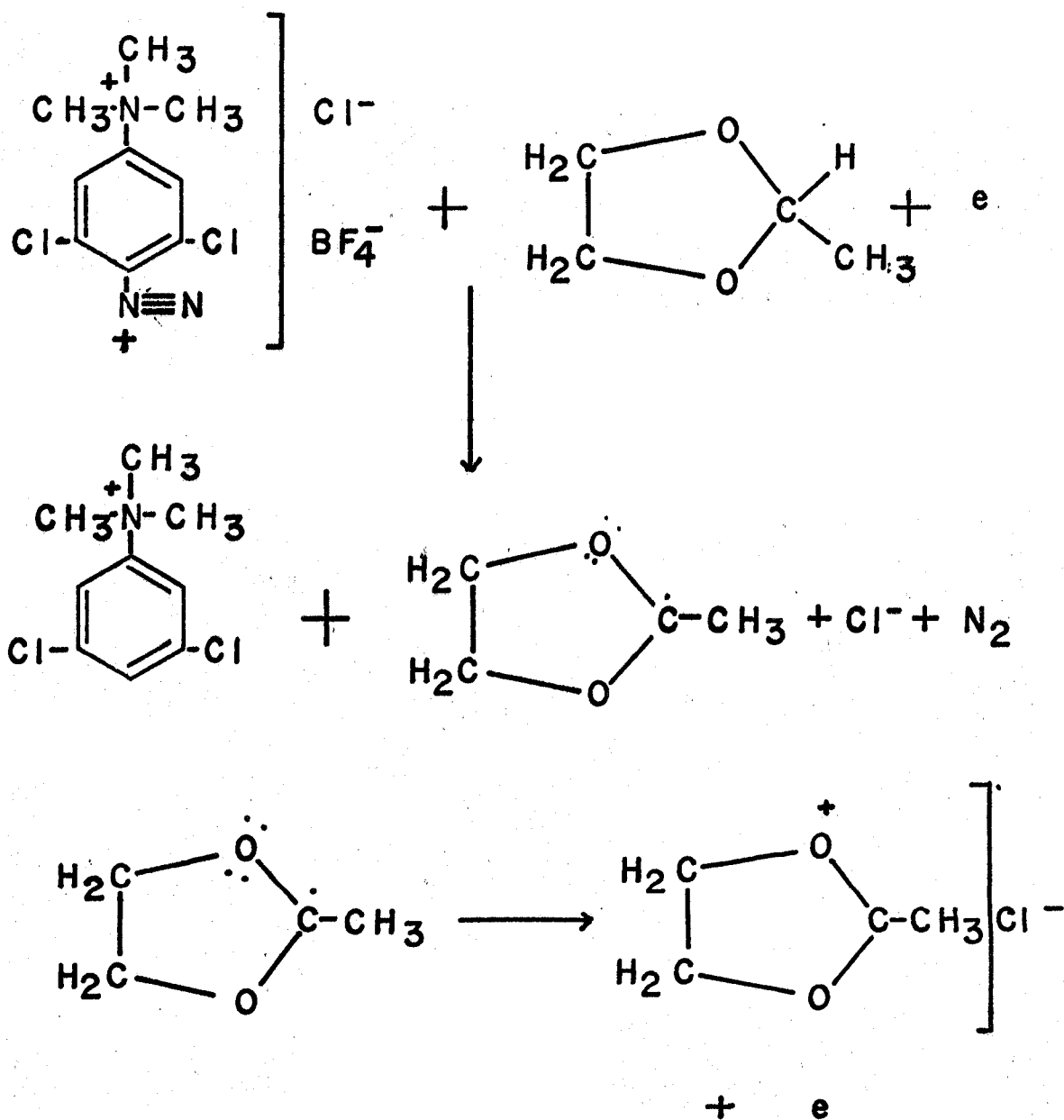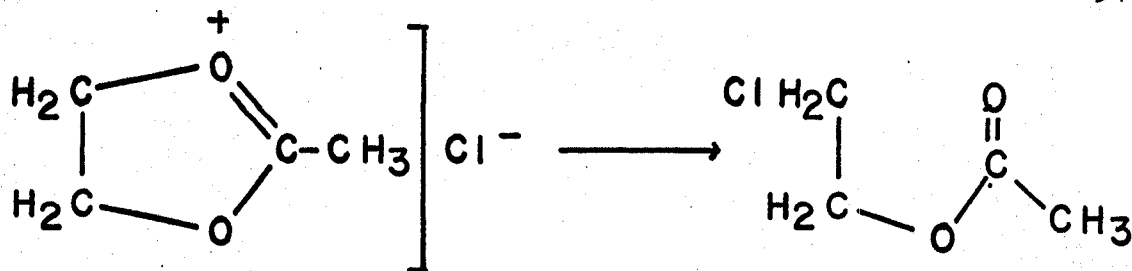
Fig. 9. The free radical reduction of 4-trimethyl-ammonium-2,6-dichlorobenzenediazonium fluoborate chloride.

All of this work by Meerwein points very strongly to a hydride transfer mechanism for the reduction of diazonium fluoborates with 1,3-dioxolanes. DeTar has given strong evidence for a hydride transfer mechanism in ethanolic deaminations. Inductive effects noted in tetramethylurea deaminations closely parallel those of the ethanolic reaction. This tends to indicate that a similar mechanism might be operative.

In tetramethylurea deaminations the aryldiazonium hexafluorophosphate presumably breaks down ionically into an aryl cation, nitrogen, and hexafluorophosphate anion. The aryl cation, depending on its reactivity, can either abstract hydride from the solvent (Fig. 10), couple with it to form a salt (Fig. 11), or react with hexafluorophosphate anion to yield the fluoroaromatic and phosphorous pentafluoride (Fig. 12). If the aryl cation abstracts hydride from the solvent as in Figure 10 the solvent ion formed
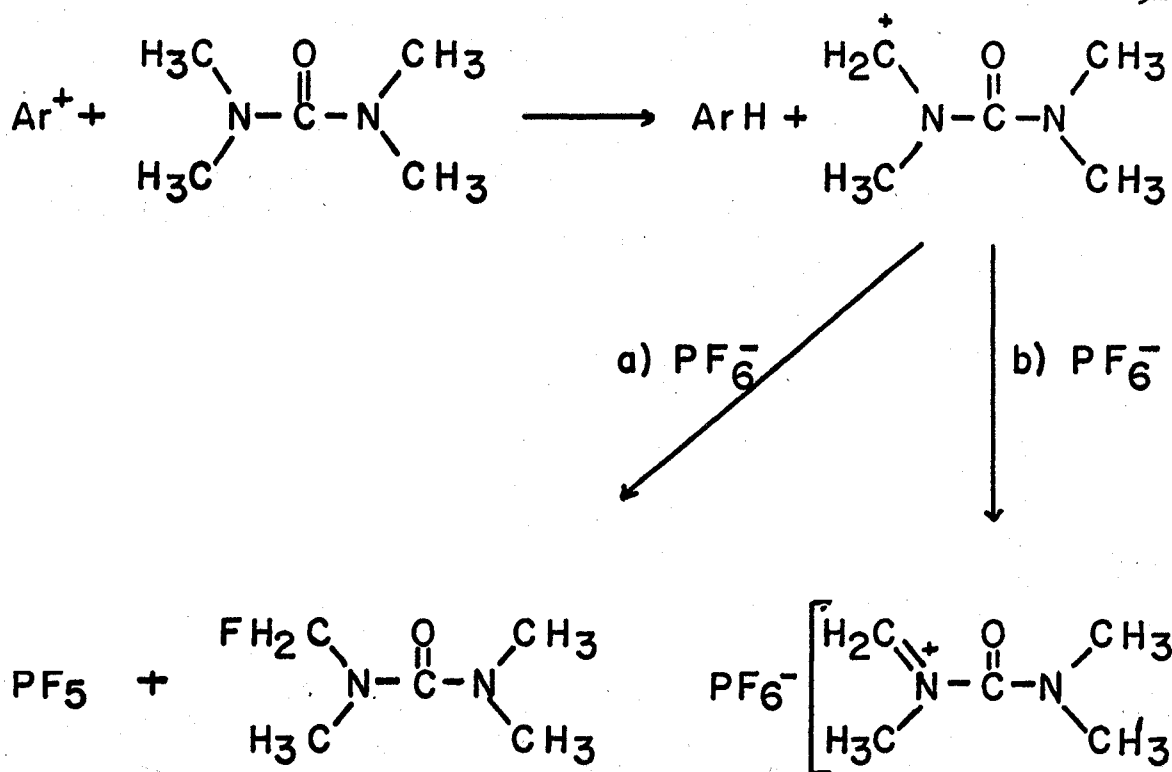
Fig. 10. The aryl cation abstracts a hydride ion from th solvent
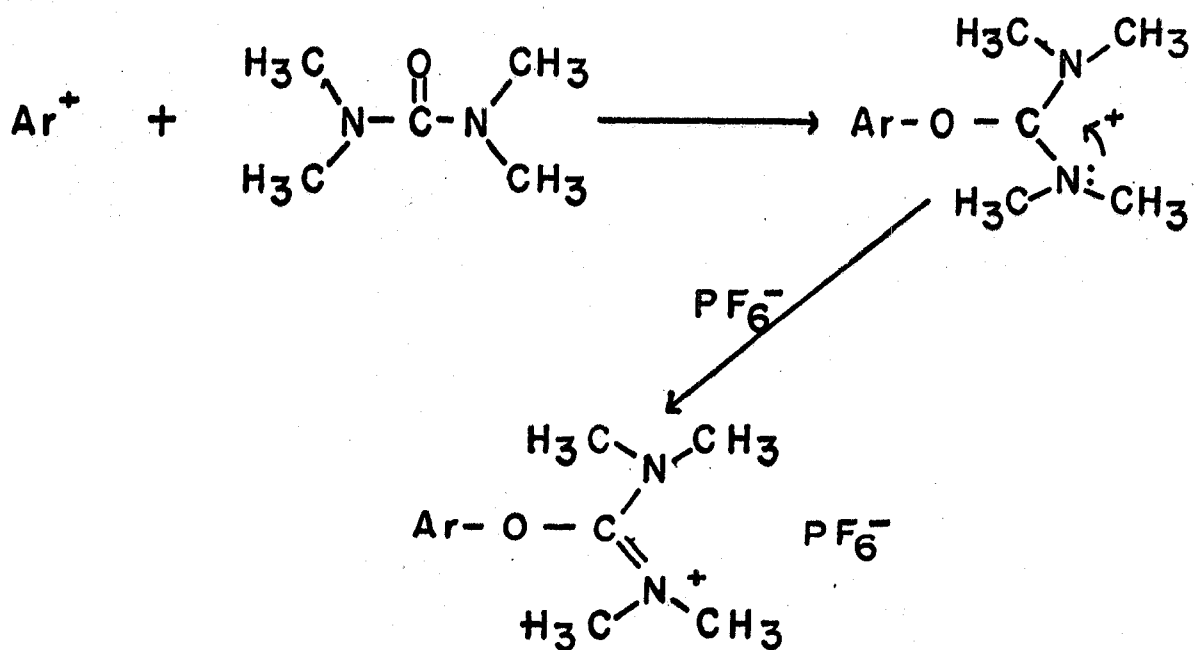
Fig. 11. The aryl cation forms a salt with the solvent.

$$Ar^+ \ + \ PF_6^- \ \longrightarrow \ ArF \ + \ PF_5$$
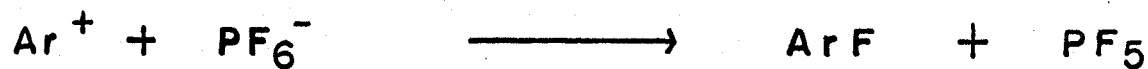
Fig. 12. The aryl cation reacts with hexafluorophosphate anion.
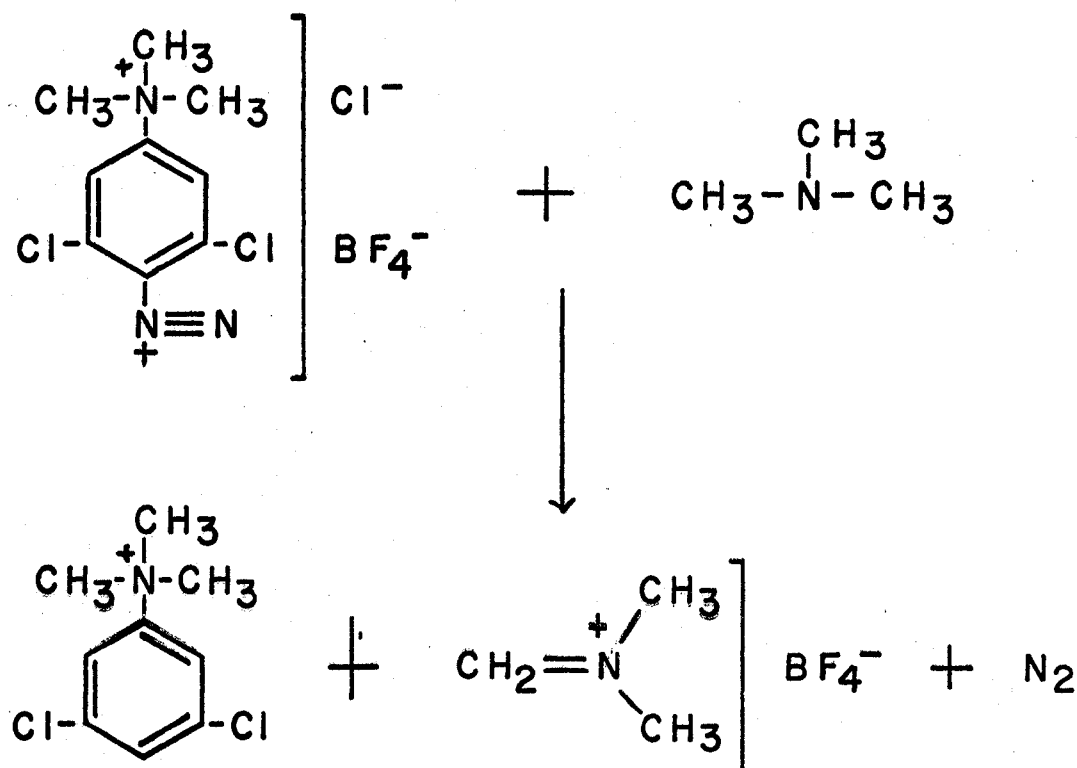
Fig. 13. The reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate chloride with trimethylamine.

may then further react either with hexafluorophosphate anion to form phosphorous pentafluoride and a fluorinated solvent molecule (Fig. 10a) or it may form a salt (Fig. 10b). The formation of a salt seems more likely since no evidence

for the evolution of phosphorous pentafluoride gas in any-
thing but trace amounts during the reaction was obtained
and because of the similarity of this pathway to that shown
by Meerwein[10] in the decomposition of 4-trimethylammonium-
3,5-dichlorobenzenediazonium fluoborate chloride in tri-
methylamine. This reaction is shown in Figure 13.

With highly reactive aryl cations, the activation
energy for hydride transfer would be met more readily and
the resultant urea carbonium ion could conceivably then
react further according to either equation shown in Figure
10a or b. However, no direct evidence has been obtained in
this laboratory for either course. No attempt was made to
isolate and characterize the products that would be obtain-
ed from either pathway even though this would give a strong
indication of the reaction mechanism. The less reactive
cations would not be sufficiently energetic for predominant
hydride transfer and competing reactions seen in Figures 11
and 12 become more likely. No evidence for reaction as in
Figure 12 has been obtained in this laboratory although it
is quite possible that small quantities of the fluoroaro-
matic may be formed in this reaction. DeTar[11] found that
small amounts of fluorocarbon were obtained in the decomp-
osition of diazonium fluoborates in methanol but no attempt
was made to show if some were formed by the decomposition

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10 H. Meerwein, K. Wunderlich, and K. F. Zenner, op.
cit.

11 D.F. DeTar and T. Kosuge, op. cit.

of diazonium hexafluorophosphates in tetramethylurea. Again
this reaction could not have occured to any large extent as
no evidence of a substantial evolution of phosphorous penta-
fluoride was obtained.

Evidence for reaction as in Figure 11, however, is con-
crete in the decomposition of o-toluenediazonium hexafluoro-
phosphate. Decomposition of this diazonium salt in tetra-
methylurea gave a 61% yield of o-methylphenoxytetramethyl-
amidinium hexafluorophosphate. The structure of this salt
(Fig. 14) was proved by elemental analysis and vigorous
base hydrolysis to o-cresol and dimethylamine. The hexa-
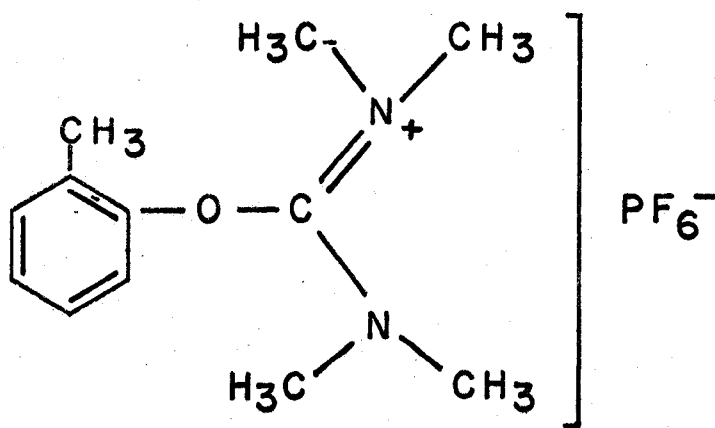
Fig. 14.   o-Methylphenoxytetramethylamidinium hexa-
fluorophosphate.

fluorophosphate anion was determined quantitatively by
tetraphenylarsonium chloride reagent.

The presence of hexafluorophosphate anion in this salt
renders a free radical reaction highly unlikely. A free
radical breakdown of the aryldiazonium hexafluorophosphate
would occur according to the equation shown in Figure 15.
To explain the evolution of nitrogen (97% of the theoretical

amount) one must envisage at least in part an electron transfer from the hexafluorophosphate anion to the positively charged nitrogen species. This would leave phosphorous pentafluoride and a fluorine atom. Regardless of the fate of the fluorine atom, reformation of the hexafluorophosphate anion would be highly unlikely. Again, an electron transfer from the solvent to the positively charged nitrogen species would render the solvent positively charged. This charged species would have a stronger tendency to react with the hexafluorophosphate anion than with the aromatic free radical. Again this would produce phosphorous pentafluoride or the hexafluorophosphate salt with the solvent.

$$ArN_2PF_6 \longrightarrow Ar\cdot + \;:N\equiv\overset{+}{N}\cdot \; + \; PF_6^-$$
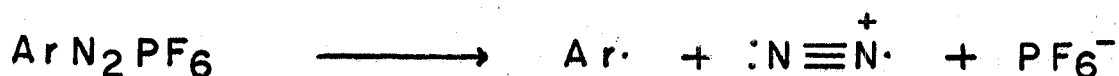
Fig. 15. Free radical breakdown of aryldiazonium hexafluorophosphates.

Similar salts as well as reduction product have been isolated from the decomposition of the diazonium hexafluorophosphate salts derived from p-nitroaniline, aniline, and p-toluidine. It is interesting to note that Meerwein[12] decomposed the diazonium fluoborates derived from p-nitroaniline and p-chloroaniline in tetramethylthiourea. No reduc-

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12 H. Meerwein, G. Dittmar, R. Gollner, K. Hofner, F. Mensch, and O. Steinfort, Ber., 90, 851 (1957).

-tion product was reported - instead there were obtained in high yields tetramethylthiouronium fluoborate salts of the following structure.

X = NO_2, Cl
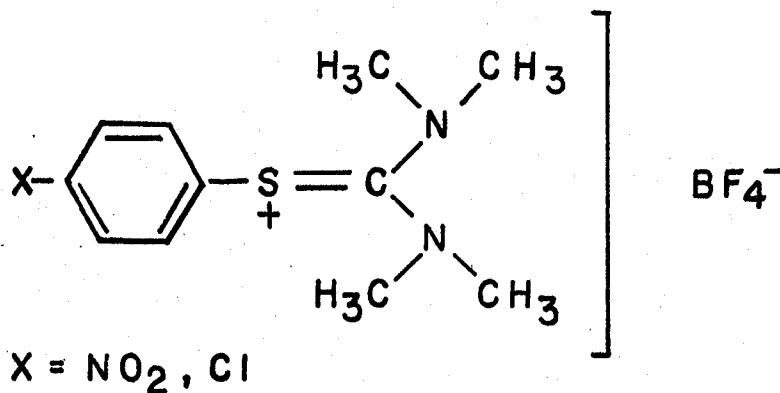
Fig. 16. Tetramethylthiouronium fluoborates.

Evidently the much higher nucleophilic property of the sulfur atom over oxygen as well as its greater size makes it more susceptible to attack by the aryl cation and hence a reaction analogous to the equation shown in Figure 11 is predominant.

CHAPTER III

EXPERIMENTAL

1. The Preparation of Aryldiazonium Hexafluorophosphates.

In all cases diazotization was carried out in the usual manner. That is, the amine was dissolved in an aqueous solution of hydrochloric acid and diazotization effected in the cold (less than $0°$) by the stepwise addition of an aqueous solution of sodium nitrite. In a few cases it was necessary to heat the amine in the hydrochloric acid solution before it would dissolve. The amine hydrochloride would then reprecipitate on cooling to diazotization temperature but as long as the hydrochloride was initially formed this had no effect on the diazotization reaction.

When an excess of nitrous acid was formed, as shown by a test with potassium iodide-starch test paper, hexafluorophosphoric acid[1] was added to precipitate the diazonium hexafluorophosphate. The precipitate was separated by filtration over suction, air dried for several hours, washed with a solution of 80 parts ether and 20 parts methanol and dried over suction. In some cases the diazonium salt was

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1. A 65% aqueous solution of hexafluorophosphoric acid (sp. gr. 1.8) obtained from Ozark-Mahoning Co. of Tulsa, Oklahoma was used.

64

further dried overnight in a vacuum desiccator. The product was then weighed and its decomposition temperature was recorded.

The general method is illustrated by the following example for the preparation of o-toluenediazonium hexafluorophosphate. For the remaining compounds only the differences in method from this example along with the quantities of reagents used, yield, decomposition temperature etc. will be given.

Toluene-2-diazonium Hexafluorophosphate.- The addition of toluidine (50g., 0.47 mole) to a solution of concentrated hydrochloric acid (100 ml., 37%) in one liter of water contained in a two-liter, wide-mouthed Erlenmeyer flask resulted in the complete formation of o-toluidine hydrochloride. The contents of the flask were cooled to -5° in an acetone-dry ice bath and diazotization effected by the addition of sodium nitrite (35 g., 0.51 mole) dissolved in 100 ml of water. The addition of the sodium nitrite solution was carried out at such a rate that the temperature of the reaction mixture did not rise above -3°. When all the sodium nitrite had been added, the presence of an excess of nitrous acid was indicated by the formation of an immediate blue coloration when potassium iodide-starch paper was wetted with the solution. While the o-toluenediazonium chloride solution was still cold hexafluorophosphoric acid (110 ml., 0.9 mole) measured in a polyproylene container was added in one portion while the reaction flask was vigorously swirled.

A white precipitate was immediately formed and the temperature of the reaction mixture rose several degrees. The mixture was again cooled to -5°, the solid was separated by suction filtration, and washed with 500 ml. of cold water. Most of the water was removed by compacting the filter cake while it was still in the Buchner funnel. (A large ground glass stopper was found to be quite effective for this purpose). The precipitate was air dried for several hours over suction and then washed with a solution which contained 80 parts ether and 20 parts methanol to aid further drying and to effect the removal of organic impurities. After it was air dried over suction for an additional hour the filter cake was powdered and weighed. A yield of 119.3 g. (97%) was obtained, m.p. 110° dec.

Toluene-4-diazonium Hexafluorophosphate.-

p-toluidine	(50 g., 0.47 mole)
hydrochloric acid	100 ml.
water	1000 ml.
sodium nitrite	35 g., 0.51 mole
hexafluorophosphoric acid	120 ml., 0.97 mole
diazotization temperature	-5°
yield	119.7 g.
percent yield	97
melting point	112° dec.

Nitrobenzene-4-diazonium Hexafluorophosphate.-

p-nitroaniline	27.6 g., 0.2 mole
hydrochloric acid	176 ml.
water	300 ml.
sodium nitrite	15 g., 0.22 mole
hexafluorophosphoric acid	45 ml., 0.36 mole
diazotization temperature	-15°
yield	55 g.
percent yield	94
melting point	156° dec.

Nitrobenzene-3-diazonium Hexafluorophosphate.-

m-nitroaniline	50 g., 0.36 mole
hydrochloric acid	300 ml.
water	500 ml.
sodium nitrite	29 g., 0.42 mole
hexafluorophosphoric acid	75 ml., 0.61 mole
diazotization temperature	-10°
yield	106.9 g.
percent yield	100
melting point	170-178° dec.

Nitrobenzene-2-diazonium Hexafluorophosphate.-

o-nitroaniline	100 g., 0.72 mole
hydrochloric acid	700 ml.
water	1000 ml.
sodium nitrite	54 g., 0.78 mole
hexafluorophosphoric acid	150 ml., 1.22 mole

diazotization temperature	$-20°$
yield	200 g.
percent yield	97
melting point	$133°$ dec.

Bromobenzene-2-diazonium Hexafluorophosphate.-

o-bromoaniline	60 g., 0.34 mole
hydrochloric acid	95 ml.
water	650 ml.
sodium nitrite	29 g., 0.42 mole
hexafluorophosphoric acid	74 ml., 0.60 mole
diazotization temperature	$-5°$
yield	120 g.
percent yield	100
melting point	$156°$ dec.

Bromobenzene-4-diazonium Hexafluorophosphate.-

p-bromoaniline	60 g., 0.34 mole
hydrochloric acid	95 ml.
water	650 ml.
sodium nitrite	29 g., 0.42 mole
hexafluorophosphoric acid	74 ml., 0.60 mole
diazotization temperature	$-5°$
yield	115.4 g.
percent yield	97
melting point	$143°$ dec.

Toluene-3-diazonium Hexafluorophosphate.-

m-toluidine	50 g., 0.47 mole
hydrochloric acid	100 ml.
water	1000 ml.
sodium nitrite	35 g., 0.51 mole
hexafluorophosphoric acid	120 ml., 0.97 mole
diazotization temperature	-3°
yield	123 g.
percent yield	100
melting point	110° dec.

Chlorobenzene-4-diazonium Hexafluorophosphate.-

p-chloroaniline	45 g., 0.35 mole
hydrochloric acid	95 ml.
water	650 ml.
sodium nitrite	29 g., 0.42 mole
hexafluorophosphoric acid	74 ml., 0.60 mole
diazotization temperature	-5°
yield	97 g.
percent yield	97
melting point	137° dec.

Anisole-2-diazonium Hexafluorophosphate.-

o-anisidine	62 g., 0.50 mole
hydrochloric acid	120 ml.
water	360 ml.
sodium nitrite	39.6 g., 0.57 mole
hexafluorophosphoric acid	75 ml., 0.61 mole

diazotization temperature -10°

yield   140 g.

percent yield   100

melting point 121° dec.

Anisole-4-diazonium Hexafluorophosphate.-

p- anisidine   60 g., 0.49 mole

hydrochloric acid   120 ml.

water   360 ml.

sodium nitrite   39.6 g., 0.57 mole

hexafluorophosphoric acid   75 ml.

diazotization temperature -10°

yield   136 g.

percent yield   100

melting point 149° dec.

Quinoline-8-diazonium Hexafluorophosphate.-

8-aminoquinoline   50 g., 0.35 mole

hydrochloric acid   150 ml.

water   300 ml.

sodium nitrite   24 g., 0.35 mole

hexafluorophosphoric acid   60 ml., 0.49 mole

diazotization temperature -5°

yield   102.5 g.

percent yield   99

melting point 144° dec.

Acetophenone-4-diazonium Hexafluorophosphate.-

p-aminoacetophenone	50 g., 0.37 mole
hydrochloric acid	150 ml.
water	350 ml.
sodium nitrite	25.3 g., 0.37 mole
hexafluorophosphoric acid	70 ml., 0.57 mole
diazotization temperature	-10°
yield	106.4 g.
percent yield	99
melting point	109° dec.

Phenol-4-diazonium Hexafluorophosphate.-

p-aminophenol	27.3 g., 0.25 mole
hydrochloric acid	75 ml.
water	150 ml.
sodium nitrite	19 g., 0.28 mole
hexafluorophosphoric acid	37.5 ml., 0.30 mole
diazotization temperature	0°
yield	45.2 g.
percent yield	68
melting point	$45-46^{\circ}$ dec.

Biphenyl-2-diazonium Hexafluorophosphate.-

o-aminobiphenyl	50 g., 0.30 mole
hydrochloric acid	150 ml.
water	700 ml.
sodium nitrite	23 g., 0.33 mole
hexafluorophosphoric acid	60 ml., 0.49 mole

diazotization temperature   -5°

yield   86.8 g.

percent yield   89

melting point   94-95° dec.

Benzoic Acid-2-diazonium Hexafluorophosphate.-

anthranilic acid   100 g., 0.73 mole

hydrochloric acid   72 ml.

water   500 ml.

sodium nitrite   60 g., 0.87 mole

hexafluorophosphoric acid   240 ml., 1.94 mole

diazotization temperature   -5°

yield   159 g.

percent yield   75

melting point   --

Benzoic Acid-4-diazonium Hexafluorophosphate.-

p-aminobenzoic acid   20 g., 0.15 mole

hydrochloric acid   100 ml.

water   240 ml.

sodium nitrite   12 g., 0.18 mole

hexafluorophosphoric acid   20 ml., 0.16 mole

diazotization temperature   -10°

yield   33 g.

percent yield   77

melting point   128-129° dec.

Pyridine-2-diazonium Hexafluorophosphate.- This diazonium

compound is very unstable and decomposes at a temperature lower than -10°. It was not isolated since it decomposed as formed to the corresponding fluoropyridine.

Diazotization was carried out by the portionwise addition of dry sodium nitrite (27 g., 0.39 mole) to 2-aminopyridine (35 g., 0.37 mole) suspended in cold (-5°) hexafluorophosphoric acid (120 ml., 0.97 mole). The reaction mixture solidified during the addition of sodium nitrite hence water (200 ml.) was added so that diazotization could be completed. The diazonium salt decomposed as formed with the evolution of phosphorous pentafluoride gas and no diazonium hexafluorophosphate was isolated. The reaction mixture was then allowed to warm up to room temperature to complete the decomposition of the diazonium salt.

2. The Preparation of Arylfluorides by the Decomposition of Diazonium Hexafluorophosphates.

In all cases except that for the preparation of 2-fluoropyridine, an identical apparatus was used for the decomposition of the aryldiazonium hexafluorophosphates. A one-liter, three-necked, round-bottomed flask was outfitted with a 500-mm. condenser or two 200-mm. condensers in series. A 300-ml. Erlenmeyer flask was attached to the other neck by means of a short length of gooch rubber tubing. A mechanical stirrer could also be inserted into the flask but in most cases no advantage was gained by its use. The apparatus was vented to an efficient fumehood to remove the

large volume of phosphorous pentafluoride that was evolved
during the decomposition. In cases in which the fluoro-
aromatic that was formed could be conveniently isolated by
distillation with steam, heavy mineral oil (Nujol, 200 ml.)
was added to the reaction flask and heated in an oil bath
to several degrees above the decomposition temperature of
the diazonium hexafluorophosphate prior to the addition of
the salt. In several cases the salt was decomposed without
a diluent. The reaction flask was heated in an oil bath to
a few degrees above the decomposition point of the salt and
the salt was added in small portions to the hot flask.
Whether or not a diluent was used the diazonium salt was
placed initially in the Erlenmeyer flask. From this flask
it could be easily added in small portions through the con-
necting tubing to the reaction vessel. The decomposition
was carried out at a rate sufficient to evolve phosphorous
pentafluoride rapidly yet without explosiveness. This
technique resulted in slightly higher yields of the fluoro-
aromatic.

When the evolution of phosphorous pentafluoride had
ceased the oil bath was removed and the reaction vessel was
cooled rapidly with cold water. A five percent solution of
sodium carbonate was poured through the condenser in order
to wash down any condensed fluoroaromatic and neutralize
the acidic reaction mixture.

The product was separated by distillation with steam.
The organic layer was separated from the aqueous solution

by means of a separatory funnel and was dried over anhyd-
rous sodium sulfate. Finally the product was distilled
from a Claisen-Vigreux flask and weighed.

The diazonium hexafluorophosphate obtained from anthr-
aniliic acid was decomposed in xylene while those from
p-aminobenzoic acid and p-aminophenol were decomposed with-
out the use of a solvent medium.

The following detailed description of the decomposition
of p-toluenediazonium hexafluorophosphate illustrates the
general method used. For all cases in which the general
procedure is the same only the pertinent data will be given.

Preparation of p-Fluorotoluene.- Toluene-4-diazonium hexa-
fluorophosphate (119.6 g., 0.45 mole) was placed in a 300-
ml. Erlenmeyer flask which was attached by means of a short
length of gooch rubber tubing to a one-liter, three-necked,
round-bottomed flask which contained 200 ml. of heavy min-
eral oil (Nujol). A 500-mm. reflux condenser was fitted to
the flask and the third neck stoppered with a glass stopper.
The apparatus was set up in an efficient fumehood and gently
lowered into an oil bath maintained at 125-130°. After a
ten minute wait to allow the mineral oil in the reaction
flask to reach the bath temperature the diazonium salt was
added in small portions to the reaction flask through the
rubber connecting tubing. After the last portion of the
salt was added the heating was maintained for an additional
five minutes to ensure complete decomposition. The heating

bath was then removed and the reaction vessel cooled in a
cold water bath. When the flask had cooled to room temp-
erature a saturated solution of sodium carbonate (400 ml.)
was added through the condenser. The condenser and Erlen-
meyer flask were removed from the reaction flask and a still
head and condenser set for distillation were attached. The
product was separated by distillation with steam, separated
from the aqueous layer of the distillate by means of a sep-
aratory funnel, dried over anhydrous sodium sulfate, and
distilled from a Claisen-Vigreux flask. A yield of 36.3 g.
(71%) of p-fluorotoluene, b.p. 117°, n_D^{26} 1.4657, was ob-
tained.

Important data for the preparation of the other fluoro-
compounds are given below. In all cases the general method
described above was followed.

o-Fluorotoluene.- o-Toluenediazonium hexafluorophosphate
(119 g., 0.45 mole) was decomposed in mineral oil at 115-
120°. The product was separated by distillation with steam,
the two layers separated and the organic layer dried over
anhydrous sodium sulfate. Distillation from a Claisen-
Vigreux flask gave 28.8 g. (58%) of o-fluorotoluene, b.p.
115-117°, n_D^{24} 1.4728.

p-Fluoronitrobenzene.- p-Nitrobenzenediazonium hexafluoro-
phosphate (50 g., 0.17 mole) was decomposed in heavy miner-
al oil at 170°. The product was isolated by distillation
with steam and separation from the aqueous layer. The

organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The product (15.1 g., 63%) was collected at 202-204°.

m-Fluoronitrobenzene.- m-Nitrobenzenediazonium hexafluorophosphate (50 g., 0.17 mole) was decomposed in heavy mineral oil at 190°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The product (13.8 g., 57%) was collected at 198-202°.

m-Fluorotoluene.- The decomposition of m-toluenediazonium hexafluorophosphate (123 g., 0.47 mole) was carried out in heavy mineral oil at 135°. The fluorotoluene produced was separated by distillation with steam and separation from the aqueous layer. The organic layer was distilled from a Claisen-Vigreux flask and the fraction which boiled at 114-118° collected. This gave a yield of 29.3 g. (58%) of m-fluorotoluene.

p-Chlorofluorobenzene.- p-Chlorobenzenediazonium hexafluorophosphate (97 g., 0.34 mole) was decomposed in heavy mineral oil at 160°. The product was separated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of p-chlorofluorobenzene was 31.8 g. (69%), b.p. 128-131°,

n_D^{20} 1.4972.

o-Fluoronitrobenzene.- The decomposition of o-nitrobenzene-diazonium hexafluorophosphate (95 g., 0.32 mole) was carried out in heavy mineral oil at 190°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of o-fluoronitrobenzene was 5 g. (ca. 10%), b.p. 210-216°.

o-Bromofluorobenzene.- o-Bromobenzenediazonium hexafluoro-phosphate (119 g., 0.41 mole) was decomposed in heavy mineral oil at 165°. The product was separated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of o-bromofluorobenzene was 46.1 g. (76%), b.p. 155-158°, n_D^{22} 1.5336.

p-Bromofluorobenzene.- The decomposition of p-bromobenzene-diazonium hexafluorophosphate (115 g., 0.40 mole) was carried out in heavy mineral oil at 160-170°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhy-drous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of p-bromofluorobenzene was 48 g. (79%), b.p. 150-153°, $n_D^{22.5}$ 1.5283.

<u>o-Fluoroanisole</u>.- o-Methoxybenzenediazonium hexafluoro-phosphate (70 g., 0.25 mole) was decomposed in heavy mineral oil at 170-175°. The product was separated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of o-fluoroanisole was 19 g. (61%), b.p. 158-160°, n_D^{26}1.4940.

<u>p-Fluoroanisole</u>.- The decomposition of p-methoxybenzene-diazonium hexafluorophosphate (84 g., 0.30 mole) was carried out in heavy mineral oil at 170-180°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of p-fluoroanisole was 26.5 g. (70%), b.p. 154-156°, n_D^{22} 1.4853.

<u>8-Fluoroquinoline</u>.- Quinoline-8-diazonium hexafluorophosphate (102.5 g., 0.34 mole) was decomposed in heavy mineral oil at 165-170°. The product was extracted with a dilute solution of hydrochloric acid, the extract neutralized with sodium carbonate and re-extracted with ether. After the ether solution was dried over anhydrous sodium sulfate the solvent was removed and the product distilled under reduced pressure (30 mm.). The fraction (5.9 g., 11.5%) which boiled at 147-149° was collected, n_D^{26} 1.5970.

<u>p-Fluoroacetophenone</u>.- The decomposition of p-acetophenone-

diazonium hexafluorophosphate (106 g., 0.36 mole) was car-
ried out in heavy mineral oil at 125°. The product was
isolated by distillation with steam and separation from the
aqueous layer. The organic layer was dried over anhydrous
sodium sulfate and distilled from a Claisen-Vigreux flask.
The yield of p-fluoroacetophenone was 5.8 g. (11.5%), b.p.
194-198°, n_D^{30} 1.5060.

p-Fluorophenol.- p-Hydroxybenzenediazonium hexafluorophos-
phate (51.4 g., 0.19 mole.) was decomposed without solvent
at 120-130°. The dark red tars that were formed were
extracted with ether and the ether solution dried over anhy-
drous sodium sulfate. The ether was removed by evaporation
and a rapid distillation carried out in an apparatus which
consisted of a distilling flask and a receiving flask con-
nected by a U tube of 15 mm. diameter. The U tube was
heated by passing a current, which was controlled by an
autotransformer, through nichrome wire wound around the
tube. The system was evacuated through a side arm from the
U tube to a vacuum pump and the receiving flask was cooled
in an ice-water bath. The contents of the distilling flask
were heated rapidly with an open flame and the product sol-
idified in the receiving flask. Very crude p-fluorophenol
(5.2 g., 18.5%) was collected.

2-Fluorobiphenyl.- The decomposition of biphenyl-2-diazo-
nium hexafluorophosphate (87 g., 0.27 mole) was carried out
in heavy mineral oil at 100°. The product was isolated by

distillation with steam and separation from the aqueous layer by filtration. The precipitate was air dried and weighed. A yield of 35 g. (69%) of 2-fluorobiphenyl, m.p. 71°, was obtained.

o-Fluorobenzoic acid.- o-Carboxybenzenediazonium hexafluorophosphate (70 g., 0.24 mole) was decomposed in xylene at 135-140°. The product was extracted with a saturated solution of sodium carbonate. After treatment with Norite the solution of sodium carbonate was poured slowly with stirring onto an excess of ice and hydrochloric acid whereupon the o-fluorobenzoic acid precipitated. A crude yield of 26 g. (78%) was obtained, m.p. 110-115°. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair yielded the pure acid, m.p. 124-125° (recorded m.p. 120-122°) neut. equiv., 138.5.

p-Fluorobenzoic acid.- p-Carboxybenzenediazonium hexafluorophosphate (33 g., 0.11 mole) was decomposed without solvent at a bath temperature of 145-155°. The product was extracted with a five percent solution of sodium carbonate and re-precipitated when the basic solution was poured slowly onto a mixture of ice and hydrochloric acid. The acid was separated by suction filtration and air dried. Re-crystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair yielded 10 g. (64%) of p-fluorobenzoic acid, m.p. 180-182°. A slight coloration of the acid was removed by treatment of a chloroform solution with Norite.

3. The Decomposition of Aryldiazonium Hexafluorophosphates
in Tetramethylurea.

The dry aryldiazonium hexafluorophosphates prepared as
previously described were decomposed by the stepwise addition
of 50 g. to a beaker which contained tetramethylurea (200
ml.) at room temperature. Usually a rapid evolution of
nitrogen was noted and the temperature of the reaction mix-
ture rose quite rapidly. In cases where the reaction was
only moderately exothermic the mixture was warmed to incre-
ase the rate of decomposition. The temperature was not
allowed to rise above 65° in any of the cases. When all
sign of reaction had ceased as evidenced by the lack of
nitrogen evolution (about $1\frac{1}{2}$ hours in most cases) the sol-
ution was poured into one liter of water. The reduction
product was normally recovered by distillation with steam
followed by separation from the water layer and distillation.
In the case of the reduction of the aminobenzoic acids the
reaction mixture was poured onto a mixture of cracked ice
and hydrochloric acid. The benzoic acid which precipitated
was then recovered by filtration.

Benzoic Acid from Anthranilic Acid.- o-Carboxybenzenediaz-
onium hexafluorophosphate (20 g., 0.068 mole) was decompos-
ed in 50 ml. tetramethylurea. The temperature of the react-
ion mixture was maintained between fifty and sixty degrees
until nitrogen ceased to be evolved. The mixture was then
poured onto ice and hydrochloric acid and the precipitate

separated by filtration. After it was dried in a vacuum desiccator a yield of 7.3 g. of crude benzoic acid was obtained. The filtrate from above was neutralized with sodium carbonate, extracted with ether in order to remove excess tetramethylurea and concentrated to a volume of 100 ml. This solution was acidified with hydrochloric acid and cooled in a refrigerator for one-half hour. The crystals which formed were separated by filtration and dried. This treatment yielded an additional gram of benzoic acid. The combined crude yield was 8.3 g. (87%), m.p. 110-118°. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave pure benzoic acid, m.p. 122°. The possibility that this product was actually o-fluorobenzoic acid was eliminated when a mixture melting point with an authentic sample of benzoic acid showed no depression.

Benzoic Acid from p-Aminobenzoic Acid.- p-Carboxybenzene-diazonium hexafluorophosphate (20 g., 0.068 mole) was added portionwise to tetramethylurea (80 ml.) in a 150-ml. beaker. No spontaneous decomposition occured until the temperature of the mixture was raised to 58-60°. The temperature was maintained between 60-70° for three hours until no more nitrogen was evolved. The solution was then poured over one liter of crushed ice which contained 50 ml. of concentrated hydrochlororic acid. The yellow crystalline solid which precipitated was separated by filtration and air-dried. A yield of 7.1 g. (86%) of crude benzoic acid

was obtained, m.p. 110-120°. Recrystallization from a
chloroform-petroleum ether (b.p. 30-60°) solvent pair gave
colourless crystals of benzoic acid, m.p. 119-121°.

Nitrobenzene from o-Aminonitrobenzene.- The diazonium salt
hexafluorophosphate (80 g., 0.27 mole) obtained from o-
aminonitrobenzene was added portionwise to tetramethylurea
(200 ml.). The temperature of the reacting mixture immedi-
ately rose but was held at or slightly below 70° by means
of an ice bath. When nitrogen ceased to be evolved the
reaction mixture was poured over one liter of ice which
contained 50 ml. of concentrated hydrochloric acid. The
nitrobenzene was separated by distillation with steam. The
distillate was extracted three times with 100-ml. portions
of ether, the ether solution dried over anhydrous sodium
sulfate, and the ether removed by evaporation. The product
was distilled from a Claisen-Vigreux flask under reduced
pressure and the fraction which boiled at 60-66° at 10 mm.
was collected. This gave a very crude product in greater
than quantitative yield. Therefore this impure product was
redissolved in ether and extracted three times with 50-ml.
portions of water to remove any tetramethylurea that may
have been entrained in the distillation. The ether layer
was again dried over anhydrous sodium sulfate and after
removal of the ether the product was distilled from a
Claisen-Vigreux flask. This treatment gave a yield of 25.3
g. (76%) of nitrobenzene. The m-dinitroderivative was

prepared according to standard procedures. Its melting point was 88-90° and no depression of the melting point was shown when a mixture melting point determination was made with an authentic sample of m-dinitrobenzene.

Another run was made in which 50 g. of the diazonium hexafluorophosphate was decomposed in tetramethylurea (200 ml.). Separation of the nitrobenzene was effected by distillation with steam of the mixture which resulted from addition of the reaction mixture to 1500 ml. of water. The distillate was extracted three times with 25-ml. portions of ether, the ether solution dried over anhydrous sodium sulfate and nitrobenzene separated by distillation from a Claisen-Vigreux flask. This technique yielded 18 g. (86%) of nitrobenzene, b.p. 204-208°, n_D^{20} 1.5510 (recorded n_D^{20} 1.5529).

Nitrobenzene from p-Aminonitrobenzene.- p-Nitrobenzenediazonium hexafluorophosphate (50 g., 0.17 mole) was added portionwise to tetramethylurea (200 ml.) contained in a 400-ml. beaker. The temperature of the mixture rose to 36° and nitrogen was evolved. After all the diazonium salt had been added the reaction mixture was warmed to 50-60° by means of a warm water bath and held in this temperature range until no more nitrogen was evolved. The reaction mixture was then poured into 1500 ml. of water and the nitrobenzene layer separated by distillation with steam. The organic layer was separated, dried over anhydrous

sodium sulfate and distilled from a Claisen-Vigreux flask. The fraction which boiled at 204-206° was collected. This gave a yield of 12.9 g. (61.7%) of nitrobenzene, n_D^{20} 1.5510.

The m-dinitroderivative was prepared. Its melting point was 91.5-92.5° and showed no depression when a mixture melting point determination was taken with an authentic sample.

Bromobenzene from o-Bromoaniline.- The decomposition of the diazonium hexafluorophosphate derived from o-bromoaniline was effected exactly as described in the general procedure outlined above. A yield of 19.5 g. (82%) of bromobenzene, b.p. 154-158°, n_D^{20} 1.5598, was obtained.

Bromobenzene from p-Bromoaniline.- The decomposition of the diazonium salt derived from p-bromoaniline was carried out as in the general method. A yield of 17.3 g. (72.4%) of bromobenzene, b.p. 154-158°, n_D^{20} 1.5574, was obtained.

Chlorobenzene from p-Chloroaniline.- p-Chlorobenzenediazonium hexafluorophosphate was decomposed in the same manner as outlined above. A yield of 14 g. (70%) of chlorobenzene was obtained, b.p. 128-134°, n_D^{20} 1.5223.

Acetophenone from p-Aminoacetophenone.- The method given above was followed for the decomposition of the diazonium salt derived from p-aminoacetophenone. Three washings with water (25 ml.) of the crude product obtained from distillation with steam were necessary in order to remove all

trace of tetramethylurea. The yield of acetophenone was
7 g. (34%) b.p. 198-202°, n_D^{20} 1.5318.

Benzene from Aniline.- The decomposition of the diazonium
salt prepared from aniline was carried out in the same man-
ner as was described previously. A yield of 4.9 g. (33%)
of benzene, b.p. 78-80°, $n_D^{21.5}$ 1.4995, was obtained.

Toluene from p-Toluidine.- The method described previously
was followed for the decomposition of the diazonium salt
derived from p-toluidine. A yield of 7 g. (30%) of toluene
was obtained, b.p. 108-112°.

Anisole from o-Anisidine.- The decomposition of the diazo-
nium salt derived from o-anisidine was carried out accord-
ing to the procedure outlined above. A yield of 6.5 g.
(33%) of anisole, b.p. 153-156°, n_D^{20} 1.5163, was obtained.

o-Methylphenoxytetramethylamidinium Hexafluorophosphate.-
o-Toluendiazonium hexafluorophosphate (20 g., 0.076 mole)
was added in small portions to tetramethylurea (60 ml.)
contained in a 150-ml. beaker at such a rate that the temp-
erature of the reacting mixture did not rise above 65°.
In order to prevent a very rapid decomposition it was some-
times necessary to cool the reaction mixture in an ice-
water bath. When evolution of nitrogen had ceased the deep
red reaction mixture was poured over a mixture of ice (150
g.) and concentrated hydrochloric acid (25 ml.). The deep
red precipitate which was obtained was recovered by filtra-

tion and air dried. Treatment of a chloroform solution of the product with Norite removed the red colour. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave 14.5 g. (60%) of colourless o-methylphenoxytetramethylamidinium hexafluorophosphate, m.p. 144-145°.

Anal. Calc'd for $C_{12}H_{19}ON_2PF_6$: C, 40.90; H, 5.44; N, 7.95; PF_6, 41.16.

Found: C, 40.57; H, 5.24; N, 7.75; PF_6, 41.04.

Hydrolysis of o-Methylphenoxytetramethylamidinium Hexafluorophosphate.- The hydrolysis of o-methylphenoxytetramethylamidinium hexafluorophosphate was accomplished in 100 ml. of 4N sodium hydroxide in a 250-ml. round-bottomed flask fitted with a reflux condenser. A rubber connecting tube was led from the top of the condenser into a gas washing bottle which was fitted with a sintered glass disc. To the washing bottle was added 150 ml. of anhydrous ether. While heating the flask at reflux temperature a gas was evolved which dissolved in the ether. After four hours the apparatus was disassembled and dry hydrogen chloride gas was bubbled through the ethereal solution. The precipitate which formed was isolated by rapid filtration and dried in vacuo. A yield of 3.2 g. (48.4%) of dimethylamine hydrochloride, m.p. 168-171°, was obtained.

Addition of dry ice to the reaction mixture resulted in the formation of a pink organic layer which when separated yielded 7.5 g. (83%) of o-cresol. The p-bromobenzene sulfonate derivative melted at 78°. A mixture melting

point determination with an authentic sample showed no depression. The dibromo derivative (m.p. 56°) likewise showed no depression in melting point when mixed with an equal portion of an authentic sample.

Analysis of o-Methylphenoxytetramethylamidinium Hexafluorophosphate for the Hexafluorophosphate Anion.- Three samples of 0.30-0.35 g. of the title compound were each dissolved in a solution of water (25 ml.) and acetone (10 ml.) by gentle warming on a steam bath. When all had dissolved tetraphenylarsonium chloride (35 ml., 4 g./250 ml.) was added to each solution. Hydrochloric acid (5 ml.) was added in order to help coagulate the precipitates. The precipitate was allowed to stand in contact with the mother liquor for one half hour and then separated by filtration through weighed , medium pore, sintered glass funnels. The samples were dried in an oven at 110° for one day, their weights were determined and the percentage of PF_6 was calculated. The average of the three determinations was 41.04%. The calculated value for the title compound is 41.16%.

BIBLIOGRAPHY

Bachman, G. B., and T. Hokama. J. Am. Chem. Soc., 79, 4370 (1957).

Barben, I. K., and H. Suschitzky. Chem. and Ind. (London), 1039 (1957).

Beaty, R. D., and W. K. R. Musgrave. J. Chem. Soc., 875 (1952).

Bergmann, E. D., and M. Bentov. J. Org. Chem., 19, 1594 (1954).

Bergmann, E. D., and S. Berkovic. J. Org. Chem., 26, 919 (1961).

Bergmann, E. D., S. Berkovic, and R. Ikan. J. Am. Chem. Soc., 78, 6057 (1956).

Bost, R. W., and L. D. Quin. J. Org. Chem., 18, 358 (1953).

Brewster, R. Q., and J. A. Poje. J. Am. Chem. Soc., 61, 2418 (1939).

Brown, D. N., D. H. Hey, and C. W. Rees. J. Chem. Soc., 3873 (1961).

Brunton, J. C., and H. Suschitzky. J. Chem. Soc., 1035 (1955).

Check, P. H., R. H. Wiley, and R. Roe. J. Am. Chem. Soc., 71, 1863 (1949).

Coleman, G. H., and W. F. Talbot. sym-Tribromobenzene, in Organic Synthesis, ed. in chief. A. H. Blatt. Coll. Vol. II. New York: John Wiley and Sons, Inc., 1943. p. 592.

Denham, J. M., and R. K. Ingham. J. Org. Chem., 23, 1298 (1958).

DeTar, D. F., and T. Kosuge. J. Am. Chem. Soc., 80, 6072 (1958).

DeTar, D. F., and D. I. Relyea. J. Am. Chem. Soc., 76, 1680 (1954).

DeTar, D. F., and T. E. Whitely. J. Am. Chem. Soc., 79, 2498 (1957).

DeTar, D. F., and Yun-Wen Chu. J. Am. Chem. Soc., 76, 1686 (1954).

Doak, G. O., and L. D. Freedman. J. Am. Chem. Soc., 73, 5658 (1951).

Doak, G. O., and H. G. Steinman. J. Am. Chem. Soc., 68, 1987 (1946).

Englert, R. D., and O. J. Sweeting. J. Am. Chem. Soc., 70, 2977 (1948).

Ferm, R. L., and C. A. VanderWerf. J. Am. Chem. Soc., 72, 4809 (1950).

Finger, G. C., and R. E. Oesterling. J. Am. Chem. Soc., 78, 2593 (1956).

Finger, G. C., F. H. Reed, D. M. Burners, D. M. Fort, and R. R. Blough. J. Am. Chem. Soc., 73, 145 (1951).

Finger, G. C., F. H. Reed, E. W. Maynert, and A. M. Weiner, J. Am. Chem. Soc., 73, 149 (1951).

Finger, G. C., F. H. Reed, and R. E. Oesterling. J. Am. Chem. Soc., 73, 152 (1951).

Finger, G. C., and R. H. White. J. Org. Chem., 23, 1612 (1958).

Fisher, E. C., and M. M. Joullie. J. Org. Chem., 23, 1944 (1958).

Fletcher, T. L., M. J. Namkung, H. Pan, and W. H. Wetzel. J. Org. Chem., 25, 996 (1960).

Freedman, L. D., and G. O. Doak. J. Org. Chem., 26, 2082 (1961).

Freedman, L. D., G. O. Doak, and L. Petit. J. Org. Chem., 25, 140 (1960).

Friedlander, P. Ber., 22, 587 (1889).

Gillis, R. B. J. Chem. Educ., 31, 344 (1954).

Gilman, H., and H. L. Yablunky. J. Am. Chem. Soc., 63, 949 (1941).

Gram, H. F., C. W. Mosher, and B. R. Baker. J. Am. Chem. Soc., 81, 3103 (1959).

Grassini, G., G. Illuminati, and G. Marino. Gazz. Chim. ital., 86, 1138 (1956). C. A., 52, 1937 (1958).

Griess, P. Phil. Trans. Roy. Soc. (London), A154, 683 (1864).

Haller, A. Ber., 18, 90 (1885).

Halliwell, H. F., and S. C. Nyberg. J. Chem. Soc., 4603 (1960).

Heacock, R. A. and D. H. Hey. J. Chem. Soc., 1508 (1952).

Head, J. D., and F. J. Jones. U. S. Pat., 2,606,183. C. A., 47, P3875 (1953).

Helin, A. F., and C. A. VanderWerf. J. Am. Chem. Soc., 73, 5884 (1951).

Hendrickson, J. B. J. Am. Chem. Soc., 83, 1251 (1961).

Heppolette, R. L., and J. Miller. J. Am. Chem. Soc., 75, 4265 (1953).

Hey, D. H., and D. G. Turpin. J. Chem. Soc., 2471 (1954).

Hodgson, H. H., and E. Marsden. J. Chem. Soc., 22 (1944).

Hodgson, H. H., and J. Walker. J. Chem. Soc.,1620 (1930).

Hudlicky, M. Collection Czech. Chem. Communs., 25, 1199 (1960).

Hughes, E. D., C. K. Ingold, and J. H. Ridd. J. Chem. Soc., 58 (1958).

Hunig, S., H. Balli, H. Nother, and H. Geiger. Ann., 628, 75 (1959).

Kaiser, C., and A. Burger. J. Am. Chem. Soc., 79, 4365 (1957).

Klassens, K. H., and C. J. Schoot. Rec. trav. chim., 72, 91 (1953).

Klassens, K. H., and C. J. Schoot. Rec. trav. chim., 71, 1086 (1952).

Klassens, K. H., and C. J. Schoot. Rec. trav. chim., 72, 178 (1953).

Kocheskov, K. A., A. N. Nesmeyanov, and N. K. Gipp. J. Gen. Chem., (USSR), 6, 172 (1936). C. A. 30, 4834 (1936).

Kornblum, N. Replacement of the Aromatic Primary Amino Group by Hydrogen, in Organic Reactions, ed. in chief. R. Adams. Vol. II. New York: John Wiley and Sons, Inc., 1944. pp. 262-340.

Kornblum, N., and D. C. Iffland. J. Am. Chem. Soc., 71, 2137 (1949).

Kosolapoff, G. M. J. Am. Chem. Soc., 76, 3222 (1954).

Lakin, A. M., and G. S. Petrova. Zhur. Obshchei Khim., 27, 2171 (1957). C. A., 52, 6297 (1958).

Lange, W., and E. Mueller. Ber., 63, 1058 (1930).

Lewis, E. S., and M. D. Johnson. J. Am. Chem. Soc., 81, 2070 (1959).

Lichtenberger, J., and A. M. Geyer. Bull. soc. Chim. France, 820 (1957).

Lichtenberger, J., and R. Thermet. Bull. soc. chim. France, 318 (1951). C. A. 46 3509 (1952).

Mai, J. Ber., 35, 163 (1902).

Makarova, L. G., and E. A. Gribchenko. Bull. Acad. Sci., URSS, Classe sci. chem., 693 (1958).

Makarova, L. G., and M. K. Matveeva. Bull. Acad. Sci., URSS, Classe sci. chem., 565 (1958).

Makarova, L. G., M. K. Matveeva, and E. A. Gribchenko. Bull Acad. Sci., URSS, Classe sci. chem., 1399 (1958).

Makarova, L. G., and A. N. Nesmeyanov. Isvest. Akad. Nauk., SSSR, Otdel. Khim. Nauk., 1019 (1954). C. A. 50, 241 (1956).

Malkevich, S. G., and L. V. Chereshkevich. Plasticheskii Massy, 4, 1 (1960). C. A. 55, 421 (1961).

Meerwein, H., K. Wunderlich, and K. F. Jenner. Angew. Chem. 74, 807 (1962).

Meerwein, H., G. Dittmar, R. Gollner, K. Hofner, F. Mensch, and O. Steinfort. Ber., 90, 851 (1957).

Meerwein, H., V. Hederich, H. Morschel, and K. Wunderlich. Ann., 635, 3 (1960).

Meerwein, H., K. Wunderlich, and K. F. Jenner. Angew. Chem., 74, 807 (1962).

Minor, J. T., and C. A. VanderWerf. J. Org. Chem., 17, 1425 (1952).

Montgomery, J. H., W. A. Yarnall, and V. A. Hoyle Jr. J. Org. Chem., 21, 28 (1956).

Nesmeyanov, A. N. Ber., 62, 1010 (1929).

Nesmeyanov, A. N., L. I. Emel'yanova and L. G. Makarova. Doklady Akad. Nauk., SSSR, 122, 403 (1958). C. A., 53, 3115 (1959).

Nesmeyanov, A. N., K. A. Kocheskov, and V. A. Klimova. Ber., 68, 1877 (1935).

Nesmeyanov, A. N., and L. G. Makarova, Bull. Akad. Sci., URSS, Classe sci. chem., 213 (1947).

Nesmeyanov, A. N., and L. G. Makarova. Doklady Akad. Nauk., SSSR, 87, 417 (1952). C. A. 48, 622 (1954).

Nesmeyanov, A. N., V. N. Vinogradova, and L. G. Makarova. Isvest. Akad. Nauk., SSSR, Otdel. Khim. Nauk., 1710 (1960). C. A., 55, 8335 (1961).

Neunhoeffer, O., and W. Rushe. Ann., 610, 143 (1957).

Newman, M. S., and R. H. B. Galt. J. Org. Chem., 25, 214 (1960).

Okuda, T., and S. Tatsumi. J. Biochem., (Tokyo), 44, 631 (1957).

Olah, G., and W. S. Tolgyesi. J. Org. Chem., 26, 2053 (1961).

Pavlath, A., and G. Olah. Acta. Chim. Acad. Sci. Hung., 10, 227 (1956).

Roe, A. Preparation of Aromatic Fluorine Compounds from Diazonium Fluoborates, in Organic Reactions, ed. in chief. R. Adams. Vol.V. New York: John Wiley and Sons, Inc., 1949. Pp. 193-228.

Roe, A., and J. R. Graham. J. Am. Chem. Soc., 74, 6297 (1952).

Roe, A., and C. E. Teague Jr. <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>73</u>, 687 (1951).

Rutherford, K. G., and W. Redmond. <u>1-Bromo-2-fluorobenzene</u>, in <u>Organic Synthesis</u>, ed. B. C. McKusick. Vol. 43. New York: John Wiley and Sons, Inc., 1963. p. 12.

Schenk, W. J., and G. R. Pellon. <u>U</u>. <u>S</u>. <u>Pat</u>. 2,563,796. <u>C</u>. <u>A</u>., <u>46</u>, P9125 (1952).

Starkey, E, B. <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>59</u>, 1479 (1937).

Wannagat, U., and G. Hohlstein. <u>Ber</u>., <u>88</u>, 1839 (1955).

Weygand, F., R. Lowenfeld, and E. F. Moller. <u>Ber</u>., <u>84</u>, 101 (1951).

Wiley, R. H., and W. A. Trinler. <u>J</u>. <u>Poly</u>. <u>Sci</u>., <u>42</u>, 113 (1960).

Wolff, M. E., and F. F. Owings. <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>25</u>, 1235 (1960).

Yagupol'skii, L. M., and V. I. Troitskaya. <u>Zhur</u>. <u>Obshchei Khim</u>., <u>31</u>, 915 (1961). <u>C</u>. <u>A</u>. <u>55</u>, 23409 (1961).

Zenitz, B. L., and W. H. Hartung. <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>11</u>, 444 (1946).

Zerweek, W., M. Schubert, and R. Fleischhauer. <u>Ger</u>. <u>Pat</u>., 901,175. <u>C</u>. <u>A</u>., <u>50</u>, P12111 (1956).

Zuber, F., E. Sorkin, and H. Erlenmeyer. <u>Helv</u>. <u>Chim</u>. <u>Acta</u>., <u>33</u>, 1269 (1950).

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    Decomposition of Aryldiazonium Hexafluorophosphates in
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    Chem., 28, 568 (1963).

    1-bromo-2-fluorobenzene, Organic Synthesis, Vol. 43,
    p. 12 (1963).

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96

Roe, A., and C. E. Teague Jr. J. Am. Chem. Soc., 73, 687 (1951).

Rutherford, K. G., and W. Redmond. 1-Bromo-2-fluorobenzene, in Organic Synthesis, ed. B. C. McKusick. Vol. 43. New York: John Wiley and Sons, Inc., 1963. p. 12.

Schenk, W. J., and G. R. Pellon. U. S. Pat. 2,563,796. C. A., 46, P9125 (1952).

Starkey, E, B. J. Am. Chem. Soc., 59, 1479 (1937).

Wannagat, U., and G. Hohlstein. Ber., 88, 1839 (1955).

Weygand, F., R. Lowenfeld, and E. F. Moller. Ber., 84, 101 (1951).

Wiley, R. H., and W. A. Trinler. J. Poly. Sci., 42, 113 (1960).

Wolff, M. E., and F. F. Owings. J. Org. Chem., 25, 1235 (1960).

Yagupol'skii, L. M., and V. I. Troitskaya. Zhur. Obshchei Khim., 31, 915 (1961). C. A. 55, 23409 (1961).

Zenitz, B. L., and W. H. Hartung. J. Org. Chem., 11, 444 (1946).

Zerweek, W., M. Schubert, and R. Fleischhauer. Ger. Pat., 901,175. C. A., 50, P12111 (1956).

Zuber, F., E. Sorkin, and H. Erlenmeyer. Helv. Chim. Acta., 33, 1269 (1950).

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1-bromo-2-fluorobenzene, Organic Synthesis, Vol. 43, p. 12 (1963).

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96